CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the components of soybean oil were firstly discussed. The catalysts used in this work were characterized to overview the differences of their characteristics and properties. Finally, the results of all experiments were expressed in each parameter, which affected the transesterification such as, methanol concentration, reaction time, amount and type of catalyst.

4.1 Characterization of Vegetable Oils

The starting material for alkali-catalyst transesterification must be free of water because it causes soap formation, which consumes the catalyst and reduced the catalyst efficiency. The resulting soap also causes an increase in viscosity, formation of gels and makes the separation of glycerol difficult. When there is a high free fatty acid content, the basicity on the catalyst is compensated by the acidity and results in catalyst deactivation. In order to complete the base catalyzed reaction to completion, a free fatty acid (FFA) value lower than 3% is needed [37]. The soybean oil used in this study was characterized by measuring some of its properties. The measurement procedure and raw data are shown in Appendix A. The results are summarized in Table 4.1.

Table 4.1 Free fatty acid and water content of soybean oil

Properties	Soy been oil
Acid Value, mg KOH/g	0.12
Moisture Content, %	1.14

The commercially available edible grade soy been oils are categorized as linoleic acid oils. These are oils that contain long-chained acids like linoleic acid at levels of about 50%. Zhenqiang et al. [10] confirmed the general information of these

oils by analyzing the fatty acid composition of the oils using gas chromatography. The results are shown in Table 4.2. It shows that the major fatty acid components in soy been oil are linoleic, oleic, and palmitic acids. The average molecular weight of soy been oil was calculated from the saponification value (S.V. = 193 mg KOH/g) as 874 g/mole.

Table 4.2 Fatty acid composition of soybean oil [10]

| Fatty acid	Composition
Palmitic acid	12.3
Stearic acid	5.8
Oleic acid	26.5
Linoleic acid	49.4
Linolenic acid	5.9
Molecular Weight, g/mole	874

The fatty acid compositions and their molecular weights were determined by HPLC. In this work, suitable column are not available and GC can not detect macromolecule such as mono-, di and triglyceride, so these two parameters were not determined in this work. Instead the values determined in the previous work as reported in Table 4.2 are used.

4.2 Characterization of Prepared Catalysts

4.2.1 Thermal Analysis

As previously reported in literature, the catalytic activity of KF/ ZnO catalyst depends upon the calcination temperature [38]. It has been observed that, for the KF loaded on ZnO samples and calcined at different temperatures, the basicity of the catalysts is initially increased with the calcination temperature and reaches the maximum at the calcination temperature of 600 °C, after which it decreases [10]. Evidently, the change in basicity changes with the calcination temperature directly affects the catalytic activity for the transesterification reaction.

In this work, TGA and DTA analysis were used to confirm the optimal calcination temperature for the alkali metal salts loaded on ZnO samples. The TGA and DTA profiles for the K_2CO_3/ZnO sample are illustrated in Figure 4.1, showing three DTA peaks in the range of 30-800 °C. The first endothermic DTA peak around 120 °C, which is accompanied by a mass loss of 3.4%, corresponds to the elimination of the surface loosely held water. It suggests that the surface physisorbed water can be removed during the cause of drying. The second DTA endothermic peak presents at 300 °C, which may be originated from combination of various decompositions of K_2CO_3. Exothermic peak found at 400 °C may be caused from solid state interaction of alkali metal with ZnO. Moreover, the profile showed approximately no weight loss after the temperature around 400°C suggesting that, from this temperature, all the residue components have been removed from the catalyst. However, the open literature [38] have reported that at 600°C the basic strength of the catalyst became higher and then gave more active catalyst for transesterificaiton. So this temperature was selected for the calcination of the corresponding ZnO.
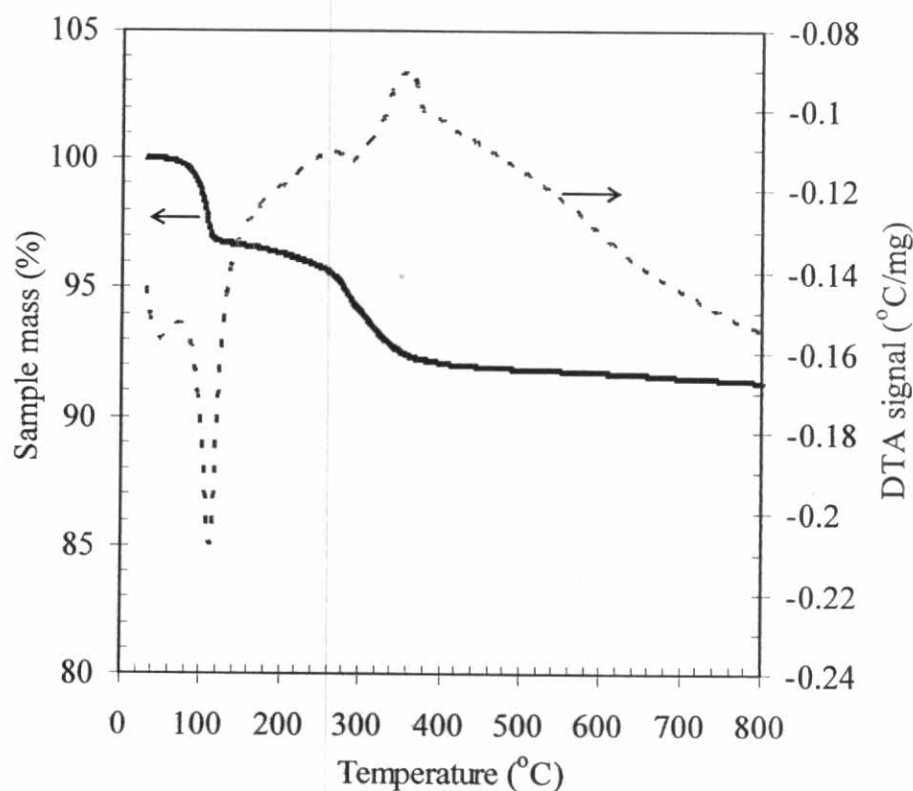

Figure 4.1 DTA-TGA profiles of K_2CO_3/ZnO sample.

4.2.2 XRD Analysis

The XRD analyses of samples have been performed to obtain more information about the catalysts structure. Figure 4.2 shows the XRD patterns of ZnO powders loaded with six different kinds of alkali metal salt (Li_2CO_3, Na_2CO_3, K_2CO_3, KOH, KCl and KNO_3) and calcinationat 600°C. XRD pattern of bare ZnO was then compared to those of calcinationZnO coated with six different salts. The XRD pattern of 15% K_2CO_3/ZnO sample is identical to that of the hexagonal wurtzite structure of pure ZnO (JCPDS 36-1451) (see curve (i) in Figure 4.2(a)). Neither characteristic peaks of K_2CO_3 (2θ = 31.6°, 32.1 ° and 37.7 °; JCPDS 16-0820) nor those for new phases such as K_2O (2θ = 31 ° and 55 ° [7]) is observed, indicating the good dispersion of K_2CO_3 on ZnO. As the amount of loaded K_2CO_3 was raised up to 30 wt%, XRD peaks of other species beside ZnO did not appear on the XRD patterns (curve (ii-iv) in Figure 4.2(a)). It is expected that amount of alkali metal salt at 30% loading is high enough to be detectable by XRD. Nevertheless, it was found that no peak was present for K_2CO_3 system. This can be explained that structure of alkali metal salts calcinationat 600 °C was changed to amorphous. Therefore, there is no peak found in XRD pattern. In addition, size and position of XRD peak of bare ZnO are not different to those of ZnO coated with K_2CO_3. Thus, the bulk structure of ZnO is not affected by the coating of K_2CO_3 and calcination process. Similar behaviors were also observed for the Li_2CO_3/ZnO, Na_2CO_3/ZnO, KOH/ZnO and KNO_3/ZnO samples (Figure 4.2(b-c)). It should be noted that there was no result for pure KOH because KOH highly adsorbed moisture and became the form that was not suitable for XRD measurement. Nevertheless, the samples loaded with KCl/ZnO show XRD patterns (Figure 4.2(f)) identical to that of parent KCl (2θ = 28.3°, 40.5° and 50.2°; JCPDS 04-0587) in addition to the pattern for ZnO. The higher the amount of loaded KCl, the higher the intensity of XRD peaks, which suggests a residual phase of KCl remaining on the composite. The structure of KCl is not changed to amorphous phase, so XRD peak of KCl can be found. Based on these XRD results, it is likely that the Li_2CO_3, Na_2CO_3, K_2CO_3, KOH and KNO_3 were well dispersed on ZnO.
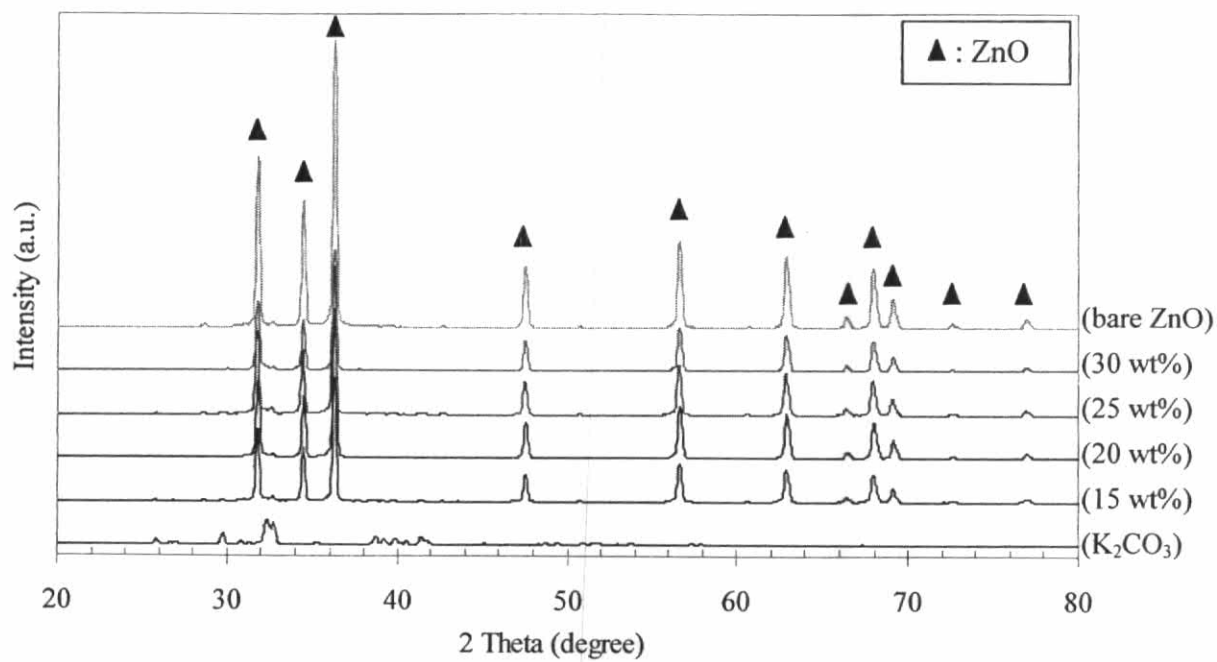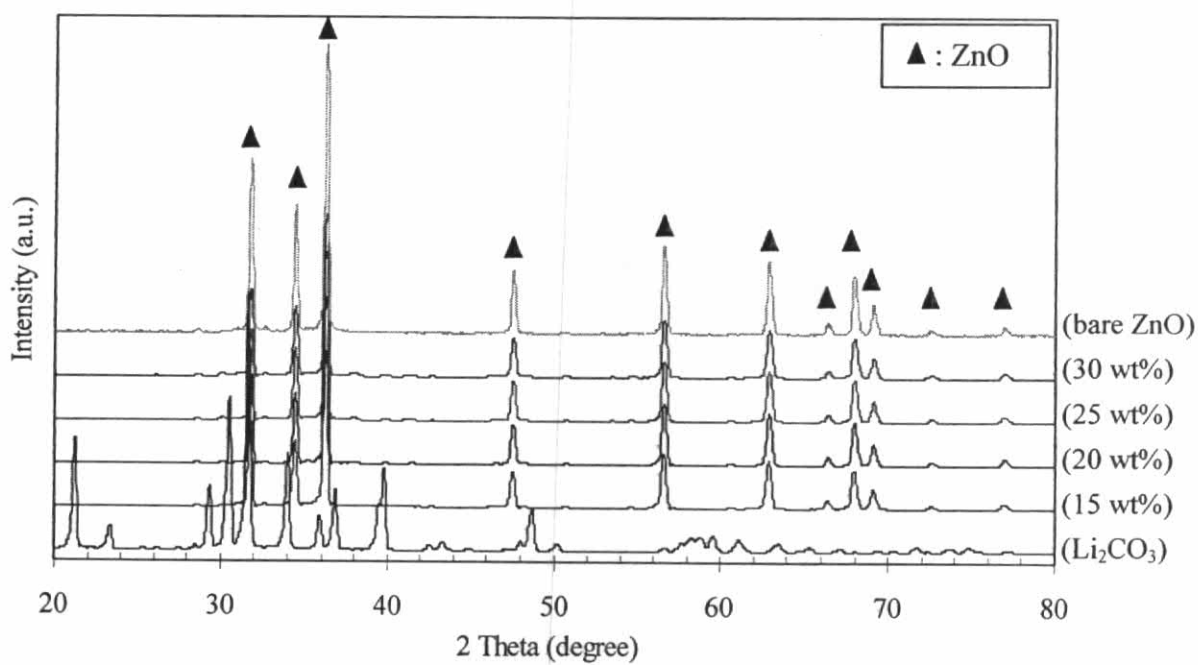
Figure 4.2 XRD pattern of ZnO loaded with K_2CO_3 (a), Li_2CO_3 (b), Na_2CO_3 (c), KOH (d), KNO_3 (e) and KCl (f), at various loading contents, after calcination at 600°C for 5 h.

(c)

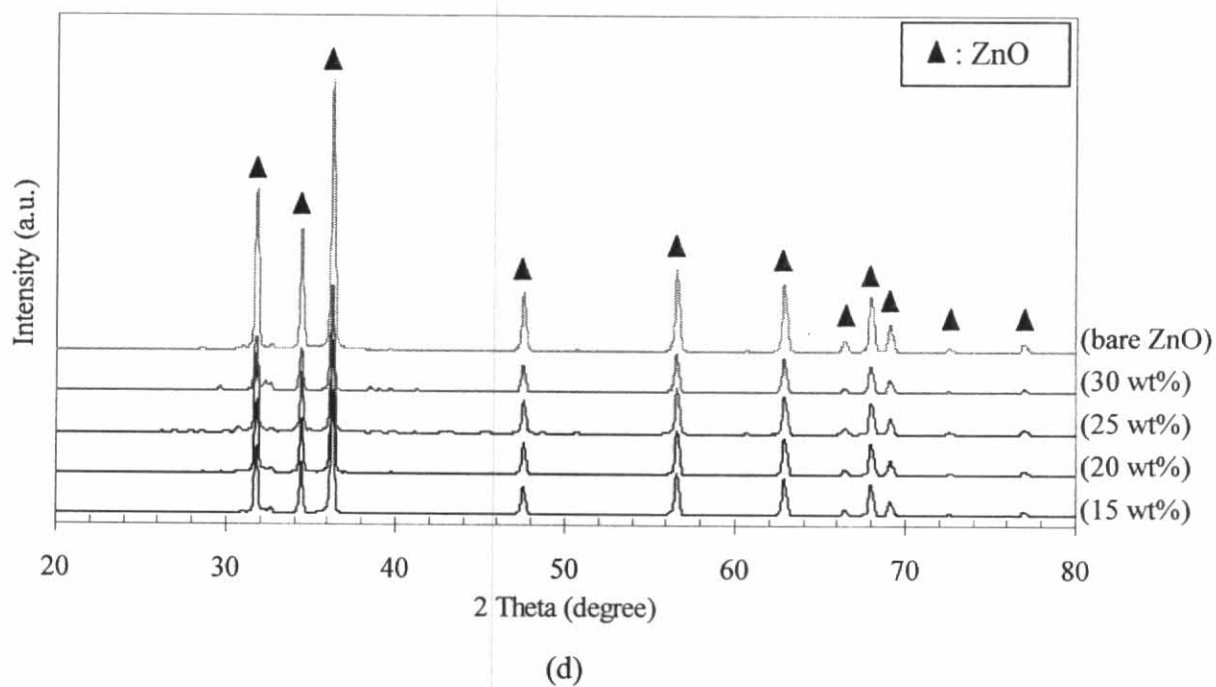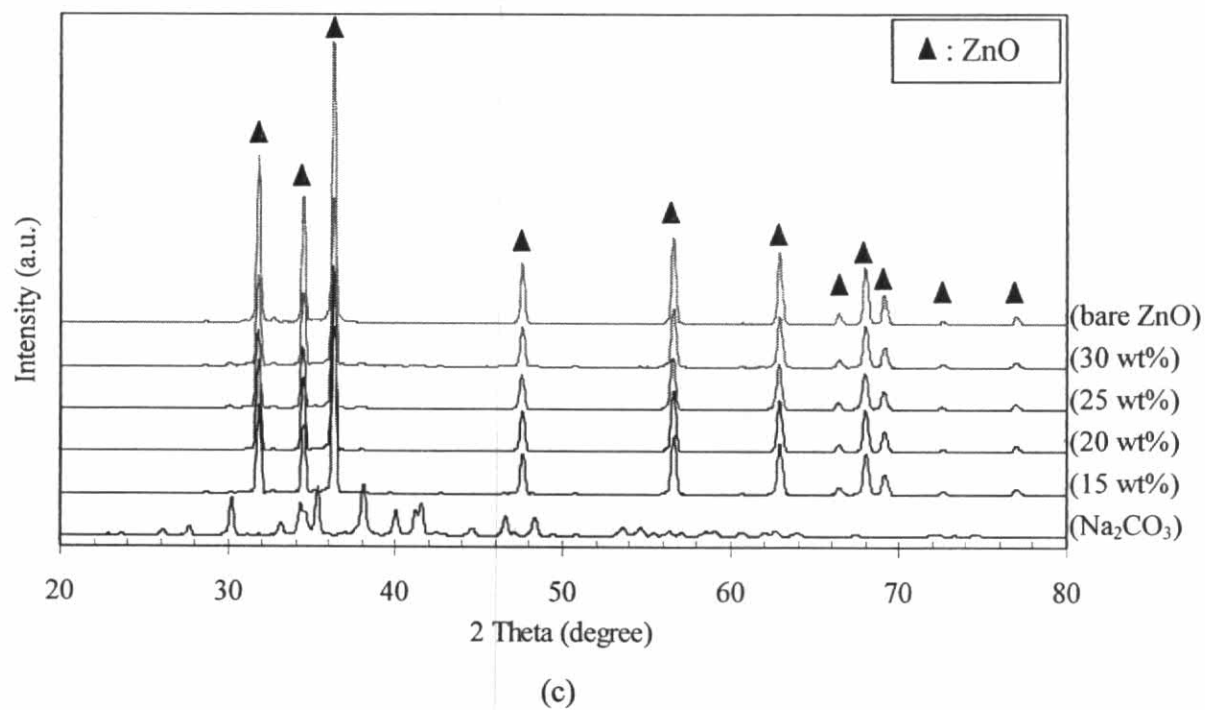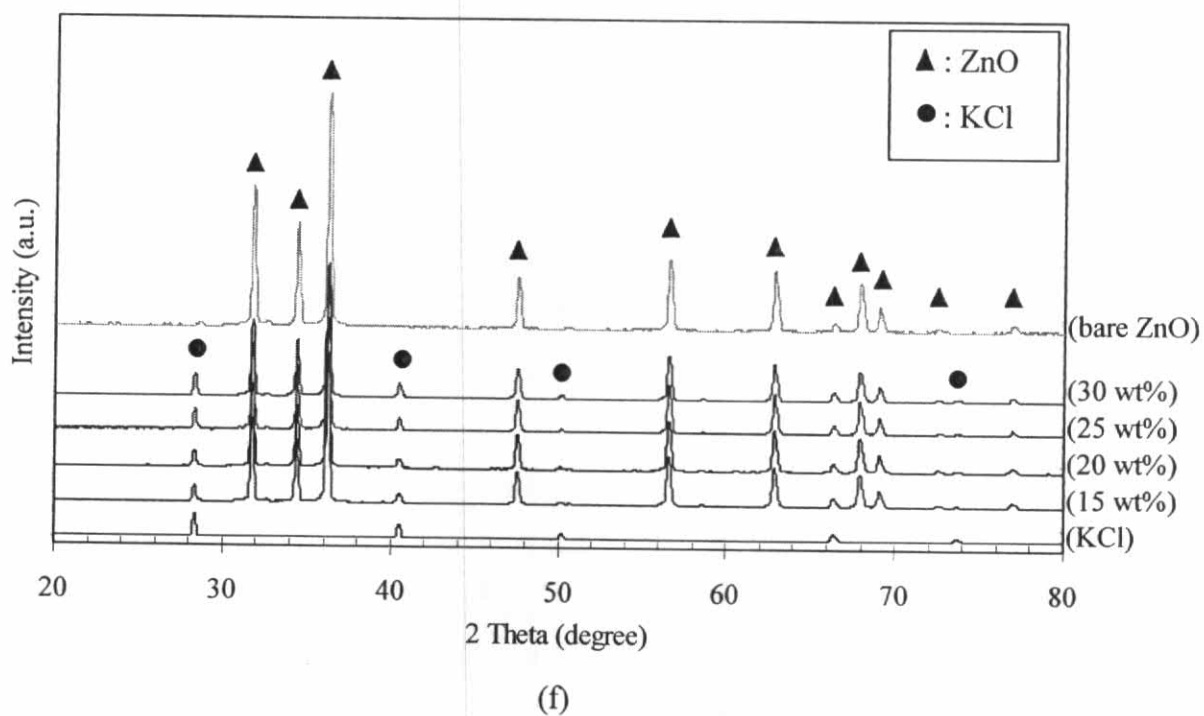(d)
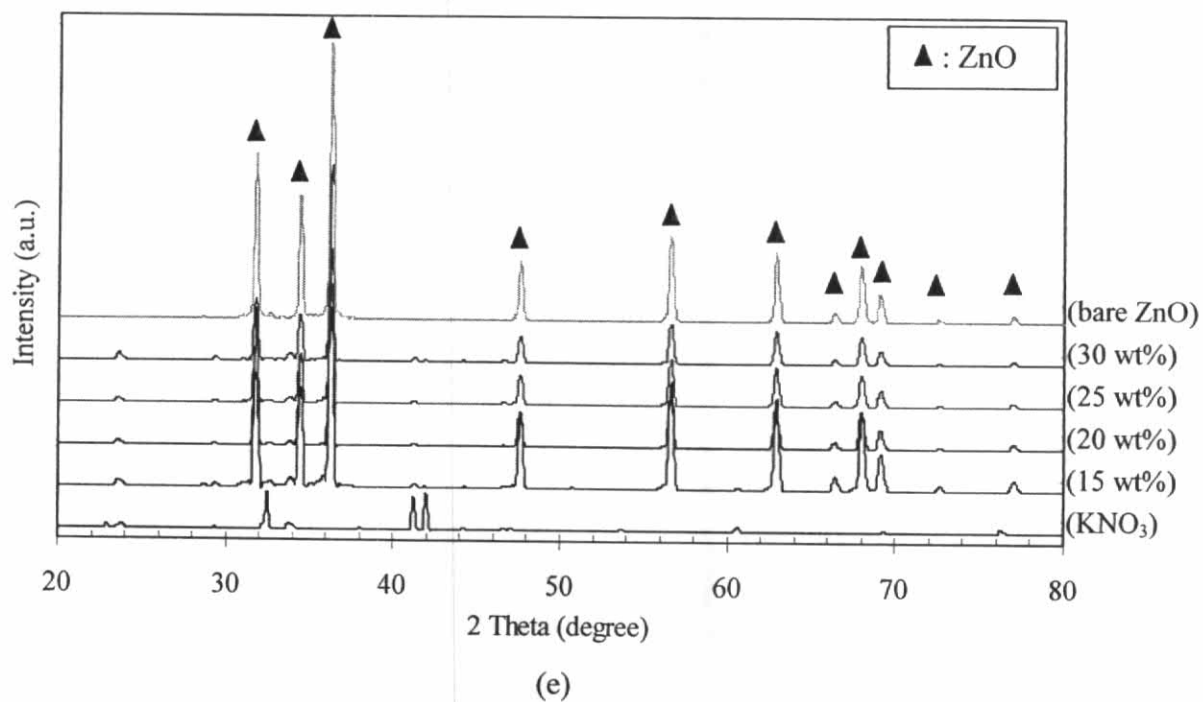
Figure 4.2 (Continued)

(e)

(f)

Figure 4.2 (Continued)

4.2.3 XPS and AA Analysis

Since FTIR graph shows that the alkali metal salt is not converted into other compounds, the difference in catalytic activity of the catalyst is the result from type and nature of the salts used for coating. In this section, the catalytic is tested by XPS technique. The loading content of 30% of salts was used because highest activity was found at this level for all prepared catalysts. However, it should be noted that the loading content described in this work was calculated based on mass of alkali metal salt, instead of the mass of the cation.

This section is, therefore, aimed to study the surface composition of the catalyst having various alkali metal salts and different percent of loading. Table 4.3 shows the surface composition of alkali metal salts-loaded zinc oxide powders prepared from incipient-wetness impregnation, characterized by X-ray photoelectron spectroscopy analysis. The XPS spectra of Zn 2p, Li 1s, Na 2s, K 2p, Cl 2p, N 1s, O 1s, and C 1s were chosen to represent the signal of elements investigated, according to their atomic sensitivity. All samples showed the presence of alkali metal on the surface and the content of them was greatly depending upon the type of their starting precursor. Based on Table 4.3, for $30\%K_2CO_3/ZnO$ system, it was found K at the surface before and after calcinations was 41.6 and 29.16%, respectively. This indicates that salt is leached from the surface into bulk solution. Amount of K found on the surface of ZnO for KOH and KNO_3 system are not different to those of K_2CO_3/ZnO system. In case of KCl system, there are very high K (50%) found on the surface of ZnO indicating that most of this salt was coated strongly on the ZnO surface. This result is in agreement with previously EDX method. For Li_2CO_3 and Na_2CO_3 systems, Li and Na were found at very low percentage. This may be caused from a low %wt of Li and Na in their salts confirmed by AA method. In addition, binding energy of K2p and Zn2p peaks shows no difference. Therefore, there are no bonds between ZnO and added salts, as confirmed by FTIR analysis.

Table 4.3 Surface composition of alkali metal -loaded ZnO characterized by XPS analysis.

| Catalyst	Peak	Position BE(eV)	Mass Concentration, (%)
30%K_2CO_3/ZnO non calcined	Zn 2p	1022	17.72
	O 1s	532	40.68
	K 2p	284.9	41.60
30%K_2CO_3/ZnO	Zn 2p	1021.9	35.00
	O 1s	531.6	35.83
	K 2p	285	29.16
30%Li_2CO_3/ZnO	Zn 2p	1022	41.98
	O 1s	532	56.36
	Li 1s	58.6	1.67
30%Na_2CO_3/ZnO	Zn 2p	1021.9	55.91
	O 1s	531.8	41.53
	Na 2s	63	2.56
30%KOH/ZnO	Zn 2p	1022.4	31.48
	O 1s	532	43.31
	K 2p	285.4	25.21
30%KNO_3/ZnO	Zn 2p	1021.9	34.98
	O 1s	531.9	36.46
	N 1s	406.7	0.41
	K 2p	285	28.15
30%KCl/ZnO	Zn 2p	1022.1	48.71
	K 2p	285	50.11
	Cl 2p	200.3	1.19

On the other hand, atomic adsorption was used to determine the bulk composition of catalyst. Table 4.4 shows the variation of alkali contents distributed through out the catalyst. Based on the best result in catalytic activity, 30% loading of salt were also used for determining Li, Na and K contents by AA method. The calculated % alkali metals in their salt were then compared to those after loading determined by AA. It was found that alkali metal found on the surface are in between 60-90% of the calculated value as shown in table 4.4. AA can not detect Li cation as described above. Even though % wt of K in chloride salt is higher than those of carbonate salt but activity of the former salt is not better than the last one. It can be concluded that activity of the catalyst does not depended on type of the alkali metal but on % loading.

Table 4.4 The composition of alkali metal -loaded ZnO characterized by AA analysis.

| Catalyst	% loaded	Mass Concentration, (%)		
		Calculated	Tested	Compared
K_2CO_3/ZnO	15	8.49	6	70.69
	20	11.32	8.4	74.23
	25	14.15	10.2	72.10
	30	16.98	12.7	74.81
KOH/ZnO	30	20.91	13	62.18
KNO_3/ZnO	30	11.60	10	86.19
KCl/ZnO	30	15.72	13.1	83.31
Li_2CO_3/ZnO	30	5.61	-	-
Na_2CO_3/ZnO	30	13.02	11.9	91.40

4.2.4 FTIR Analysis

The KBr pellet technique was applied for determining FT-IR spectra of the samples after calcination at 600°C. Figure 4.3 shows IR spectra of pure ZnO and ZnO coated with six different alkali metal salts. Strong adsorption peak of Zn-O stretching was found at 400-600 cm^{-1} for all systems. The IR peak around 2370 cm^{-1} assigned to the C=O of carbon dioxide was also exhibited for all samples. This presents the basicity of all prepared catalysts. The basicity was then re-checked with CO$_2$-TPD.
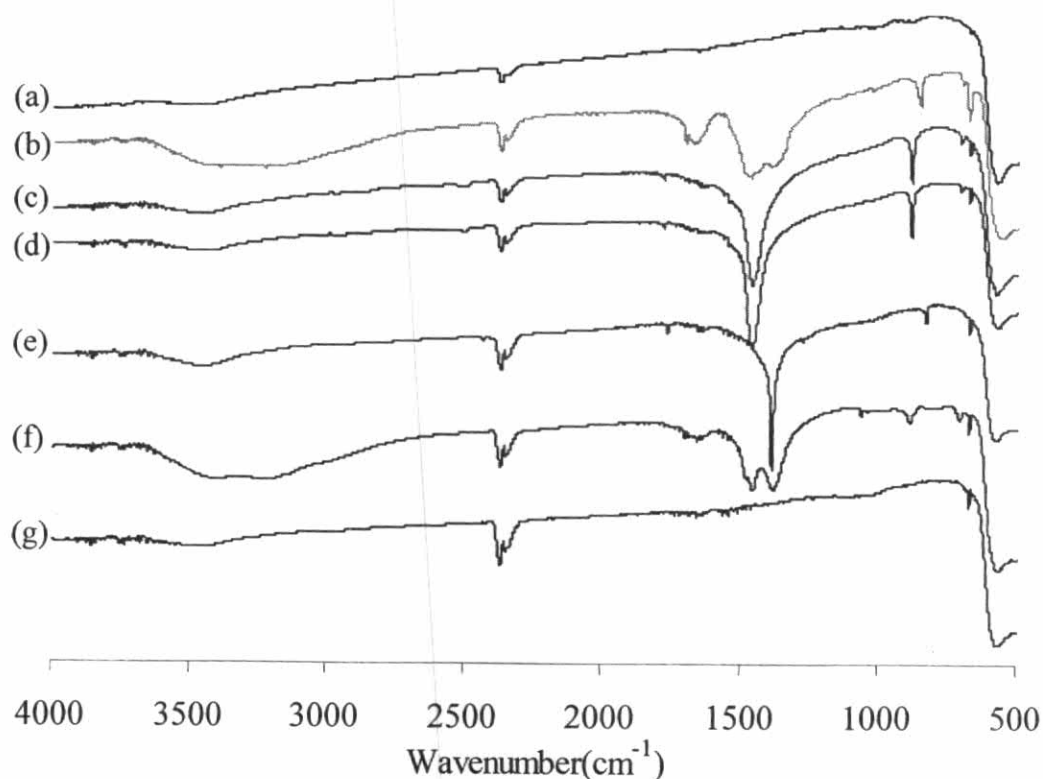

Figure 4.3 FTIR spectra of: (a) unloaded ZnO commercial powder, (b) 30%K$_2$CO$_3$/ZnO, (c) 30%Li$_2$CO$_3$/ZnO, (d) 30%Na$_2$CO$_3$/ZnO, (e) 30% KNO$_3$/ZnO, (f) 30%KOH/ZnO and (g) 30%KCl /ZnO.

Further more, FTIR spectra of six alkali metal salts coated on ZnO after calcination were compared to their pure states. It was found that IR bands for both states were similar. The same position of the IR adsorption bands were found for pure alkali metal salt and ZnO coated with the salt. It can be said that there is no any chemical bonding between salt and ZnO, i.e. the salt was just physically coated on the surface. After the modification of ZnO with basic compounds, the spectra showed interestingly the alternation of ZnO characteristics as noticed from the appearance of the spectra around 1300-1600 cm^{-1}. These were clearly similar to the spectra of free basic compound after calcination at the same temperature, regardless of the 30%KCl /ZnO which showed the similar spectra as bare ZnO. It should be noted that there is no result for pure KOH presented in Figure 4.4(d) because of the same reason mentioned in XRD analysis.

FTIR spectra of KF/Al_2O_3 before and after calcinations were studied by Weinstock et al. Lacking of intensity of adsorption peak of O-H bending of H_2O at 1640 and 3350 cm^{-1} was found. It can be explained that KF can introduce hydroxyl at the surface of Al_2O_3. O-H band at 3350 cm^{-1} was also found for K_2CO_3/ZnO system before and after calcinationas shown in Figure 4.4(a). O-H band may not only be influenced from water molecules but also the adsorption of surface hydroxyl group. Because of the lacking of O-H bending at 1640 cm^{-1} from the calcined catalyst, it is indicated, this that surface hydroxyl may be responsible for the activities of the catalysts. The result of K_2CO_3 and KOH which are the most effective basicity and activity in catalysis will be described in the next part.
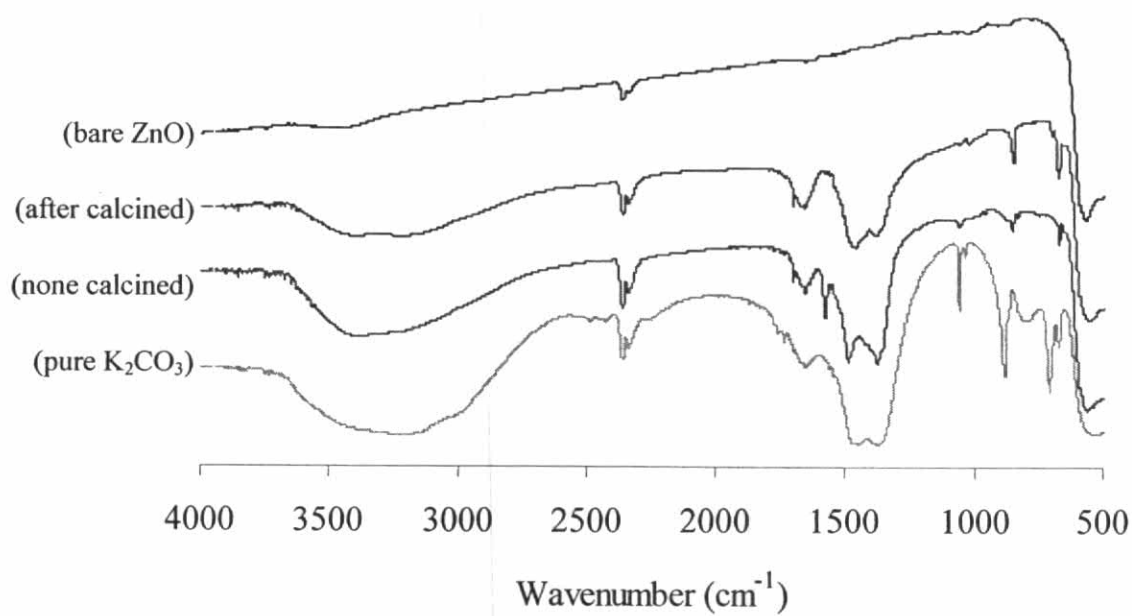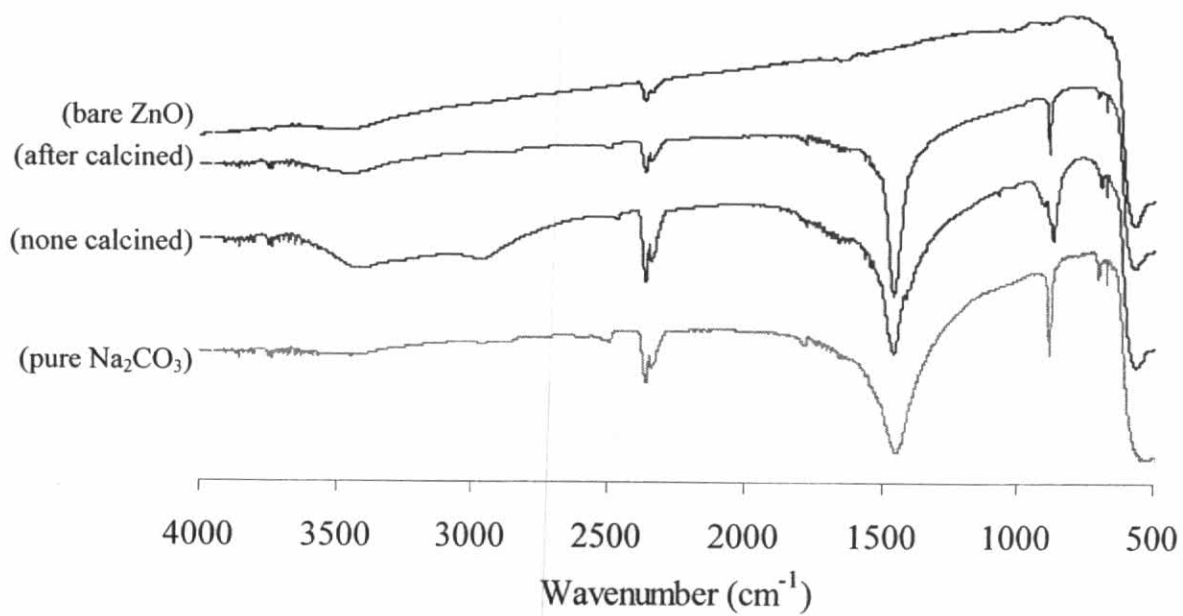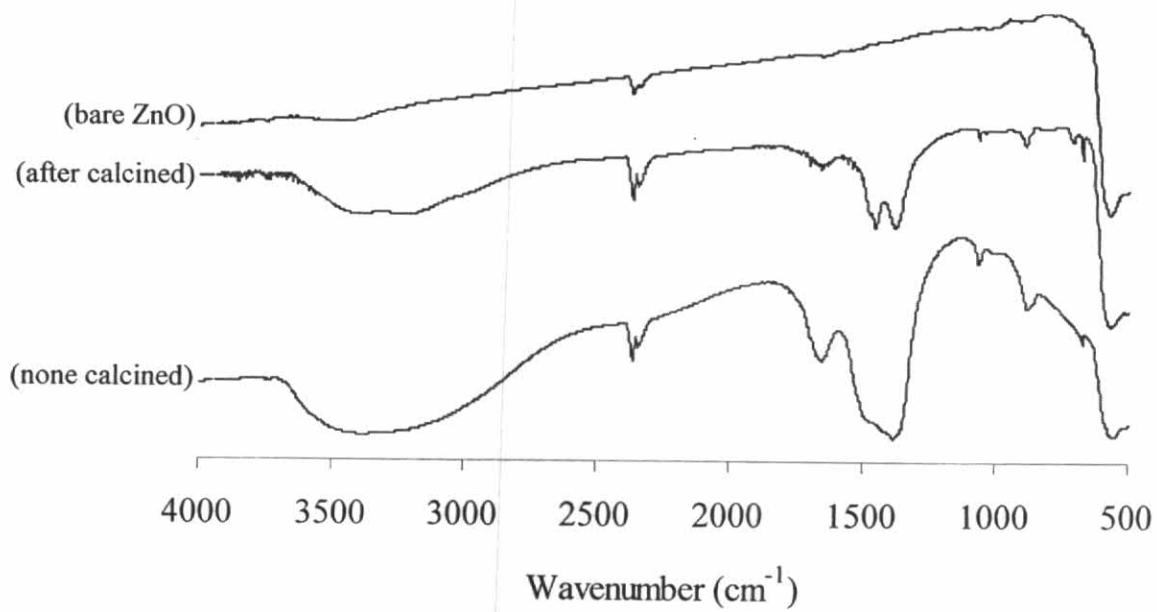
(a)
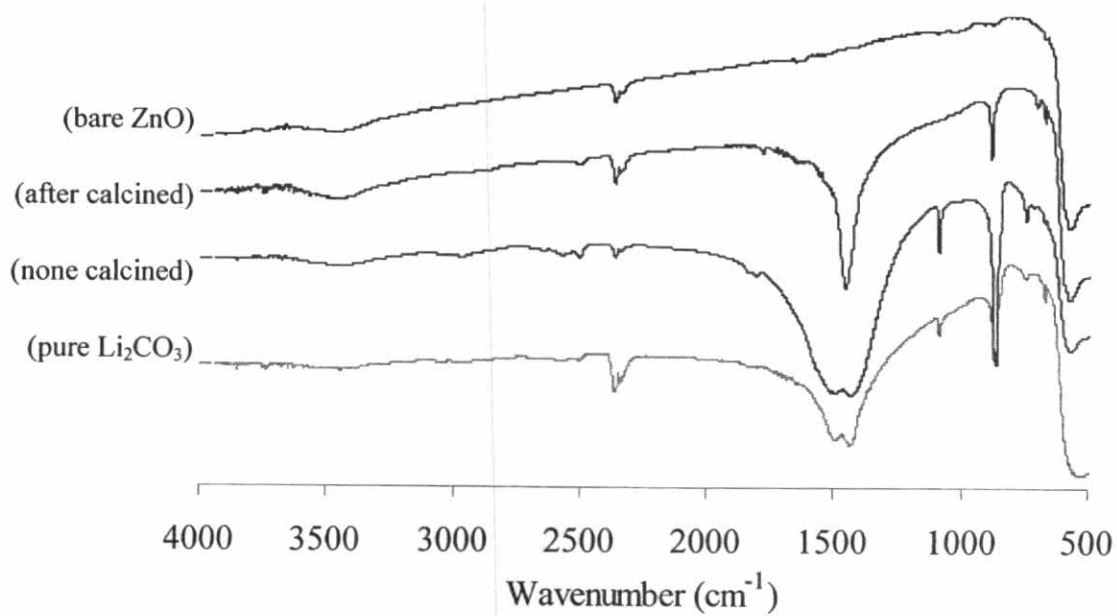
(b)

Figure 4.4 FTIR spectra of: (a) 30%K$_2$CO$_3$/ZnO, (b) 30%Li$_2$CO$_3$/ZnO, (c) 30%Na$_2$CO$_3$/ZnO, (d) 30%KOH/ZnO, (e) 30% KNO/ZnO and (f) 30%KCl /ZnO.
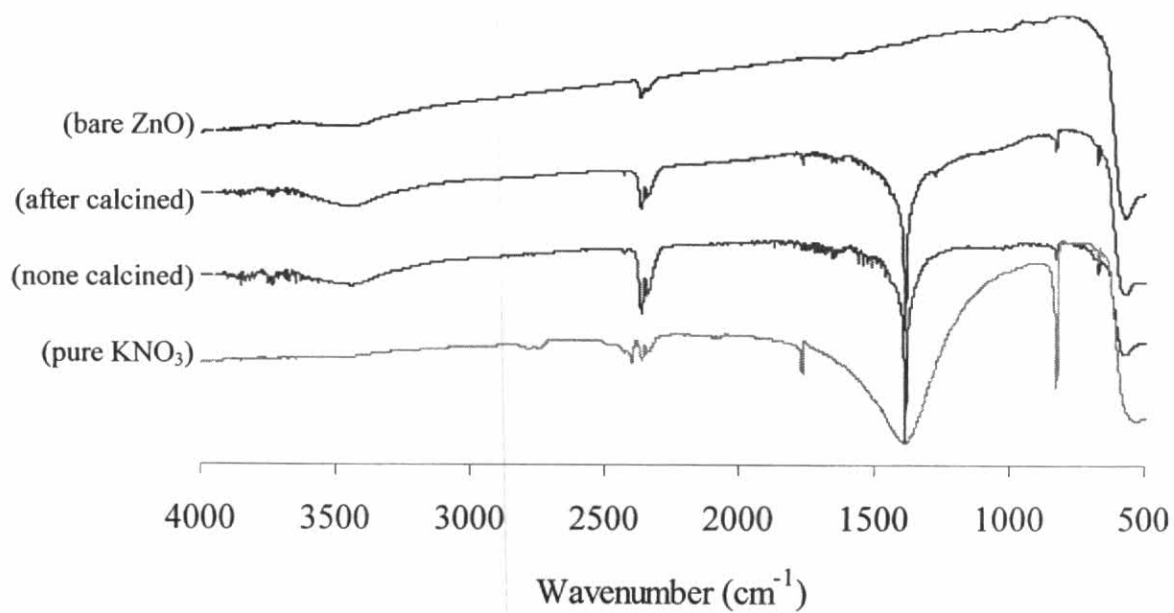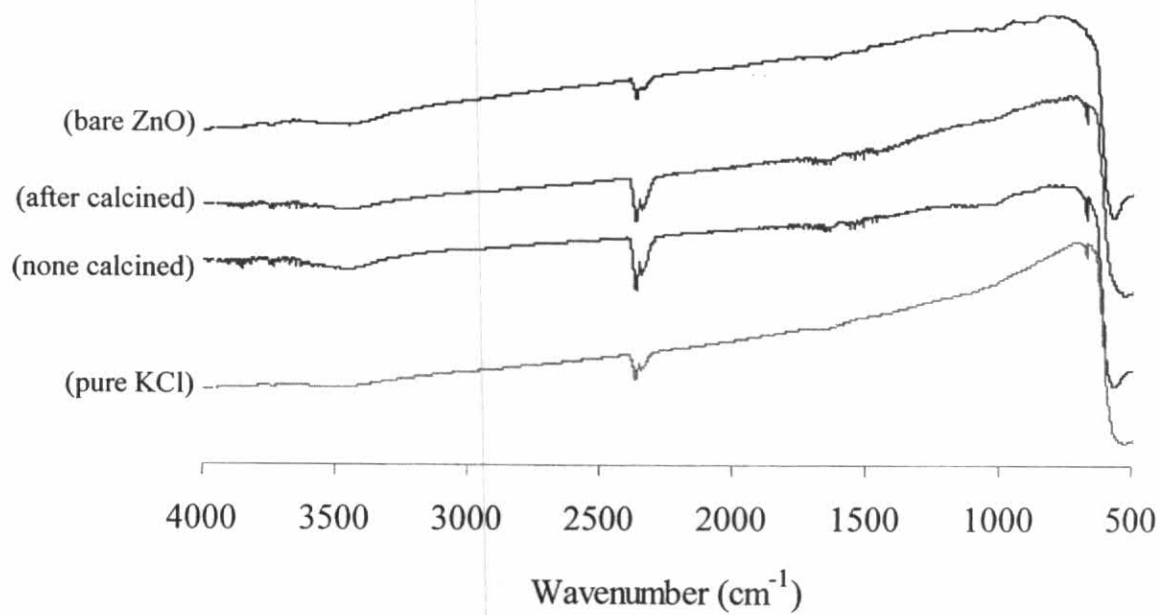
(c)

(d)

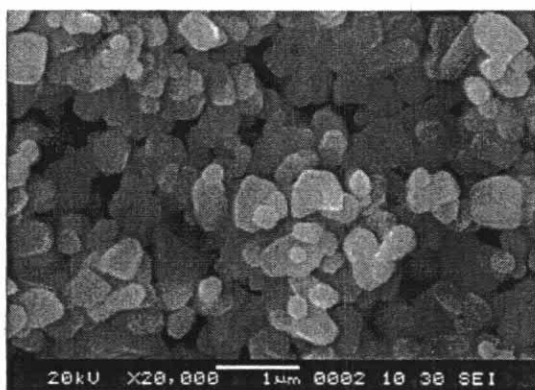**Figure 4.4** (Continued)

(e)

(f)

Figure 4.4 (Continued)

4.2.5 SEM and EDX Analysis

Scanning microscopy was used for the examination of the topology of catalyst surfaces and morphologies. Figure 4.5 shows the scanning electron micrographs of bare commercial ZnO powder and alkali metal salts-loaded ZnO catalyst. In Figure 4.5(a), if shows that the commercial ZnO powder is comprised of large number of agglomerates. Each particle is nearly of ellipsoidal shape with the length shorter than 200 nm and diameter smaller than 100 nm. In Figure 4.5(b), structure of ZnO before and after loading of K_2CO_3 and calcination are not different. This phenomenon supported the distribution of K_2CO_3 on ZnO surface as confirmed by EDX signal of K. The sizes of ZnO particles coated with different alkali metal salts are slightly different as shown in Figure 4.5 (b-h). Alkali metal salt forms multi-layers on ZnO surface. Difference in density and particle sizes of alkali metal salts directly affect the size of the aggregates. Salt with low density possesses high volume and can be adsorbed more thickly than those of high density one.

(a) (b)
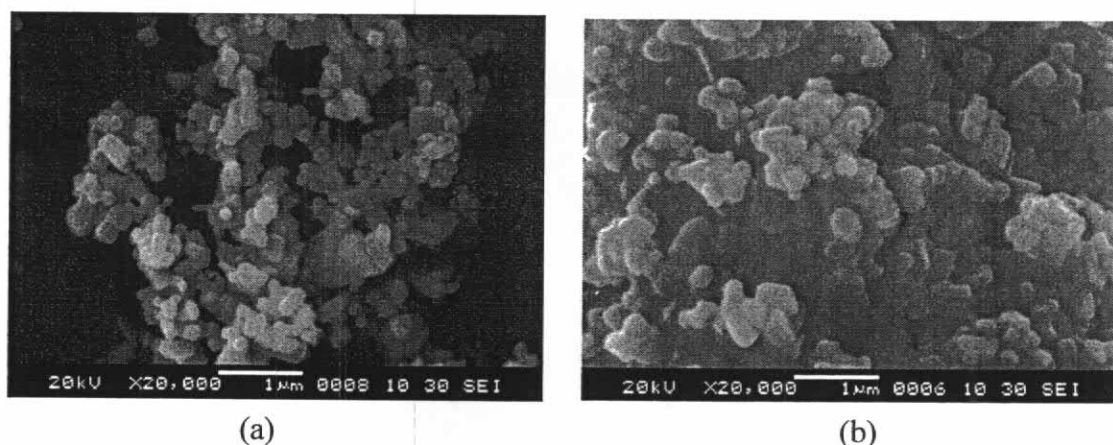
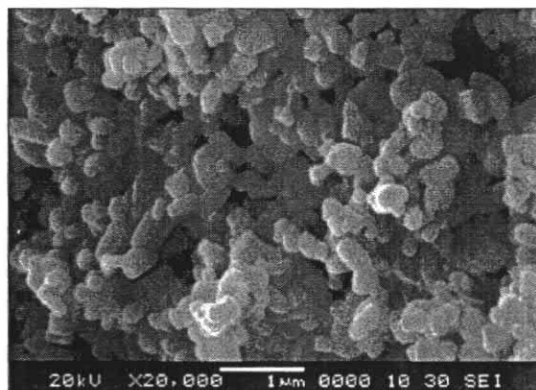**Figure 4.5** Scanning electron micrographs of: (a) bare ZnO commercial powder, (b) ZnO powder loaded with 30%K_2CO_3 before calcination, (c) 30%K_2CO_3/ZnO, (d) 30%Li_2CO_3/ZnO, (e) 30%Na_2CO_3/ZnO, (f) 30%KOH/ZnO, (g) 30% KNO_3/ZnO, and (h) 30%KCl/ZnO. It should be noted that catalysts shown in (c)-(h) were calcinationat 600°C for 5 h.

(c)

(d)
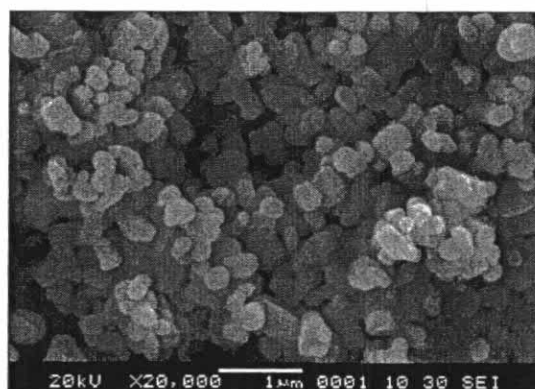
(e)
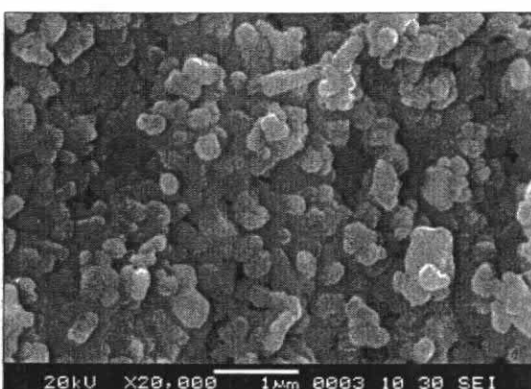
(f)
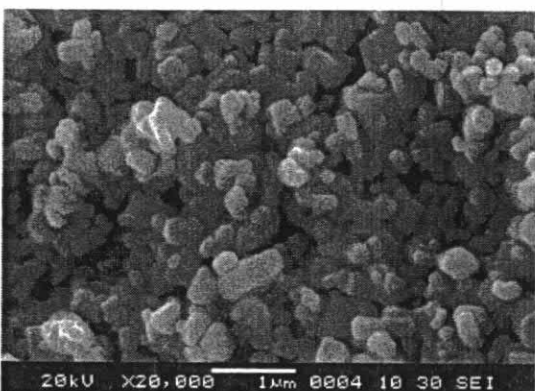
(g)
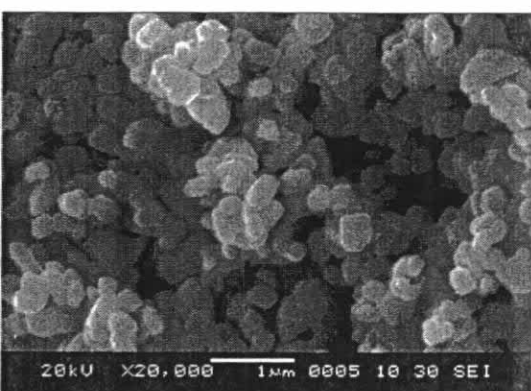
(h)

Figure 4.5 (Continued)

Based on these results, after loading of K_2CO_3, ZnO retained its structure. It was also found from EDX result, as shown in Figure 4.6, that potassium was uniformly distributed on the surface of the ZnO support. Similar results were observed for the KOH/ZnO and KNO_3/ZnO samples as well. Energy of Li cation at K_α level is 0.0544 which is very low and can not be detected by EDX. K_α (1.0410) and L_α (1.0118) of Na and Zn cations are very close in energy. Therefore, EDX shows only energy pattern of Zn cation. Moreover, the absence of Li on the ZnO surface was contributed to the limitation of EDX device on the measurement of low energy level of electron while the overlap energy level of Li and Zn made the system much more complicated to determine the exact amount of Li which can not be distinct by their energy level.

Electron Image 1
K Ka1
Zn Ka1

(a)
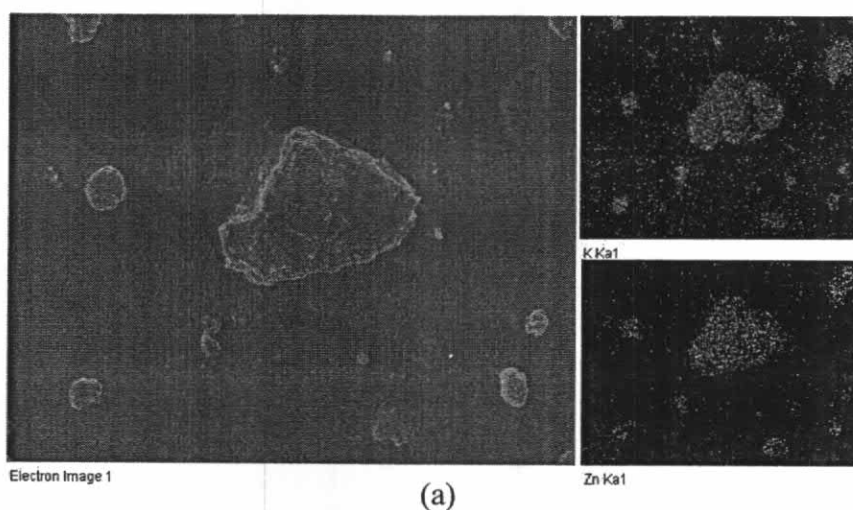
Figure 4.6 EDX elemental mapping of: (a) ZnO powder loaded with 30%K_2CO_3 before calcination, (b) 30%K_2CO_3/ZnO, (c) 30%Li_2CO_3/ZnO, (d) 30%Na_2CO_3/ZnO, (e) 30%KOH/ZnO, (f) 30% KNO_3/ZnO, and (g) 30%KCl/ZnO. It should be noted that catalysts shown in (b)-(g) were calcinationat 600°C for 5 h.

Electron Image 1

K Ka1

Zn Ka1

(b)

Electron Image 1

Zn Ka1

(c)

Electron Image 1

Zn Ka1

(b)

Figure 4.6 (Continued)

Electron Image 1

K Ka1

Zn Ka1

(f)

Electron Image 1

K Ka1

Zn Ka1

(e)

Electron Image 1

K Ka1

Cl Ka1

Zn Ka1

(g)
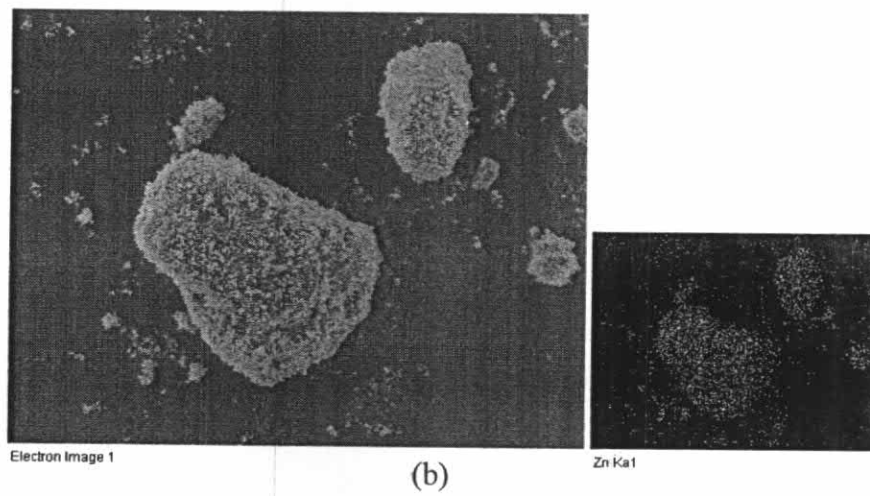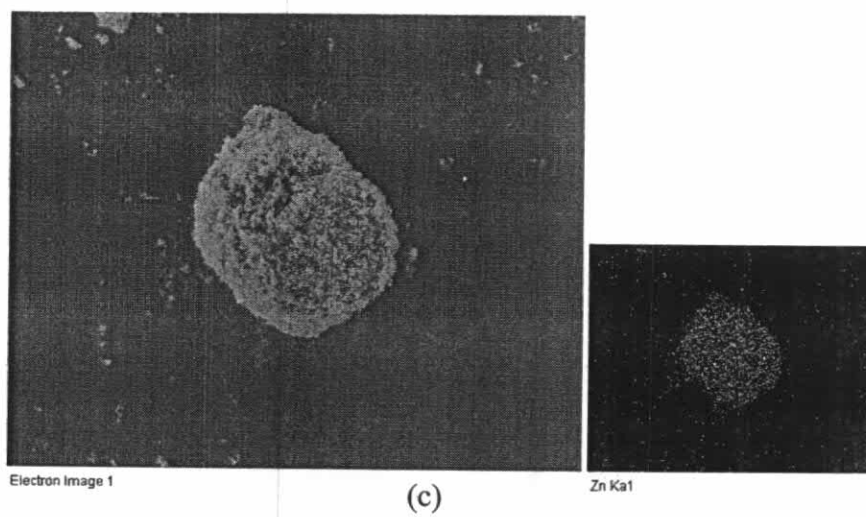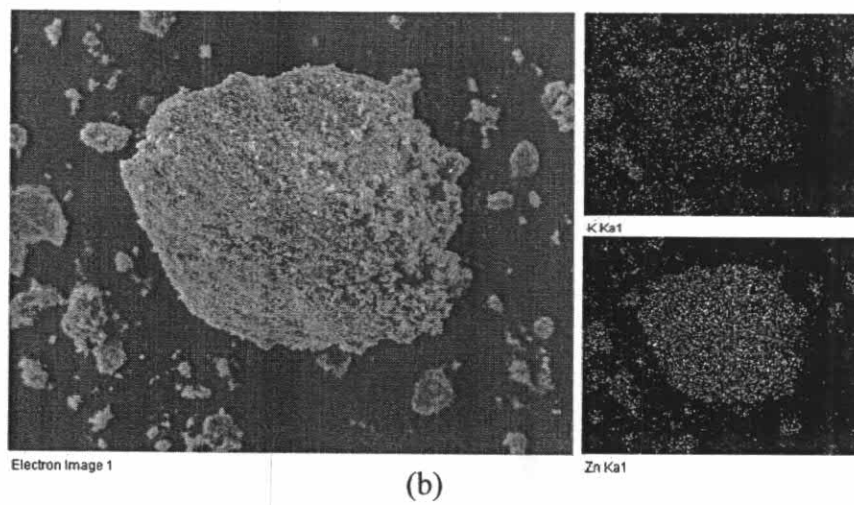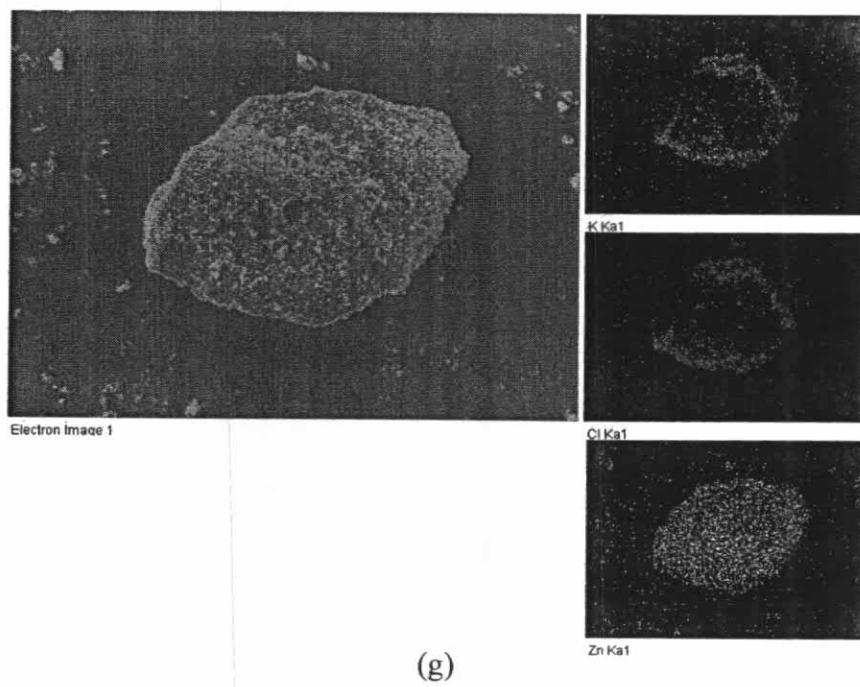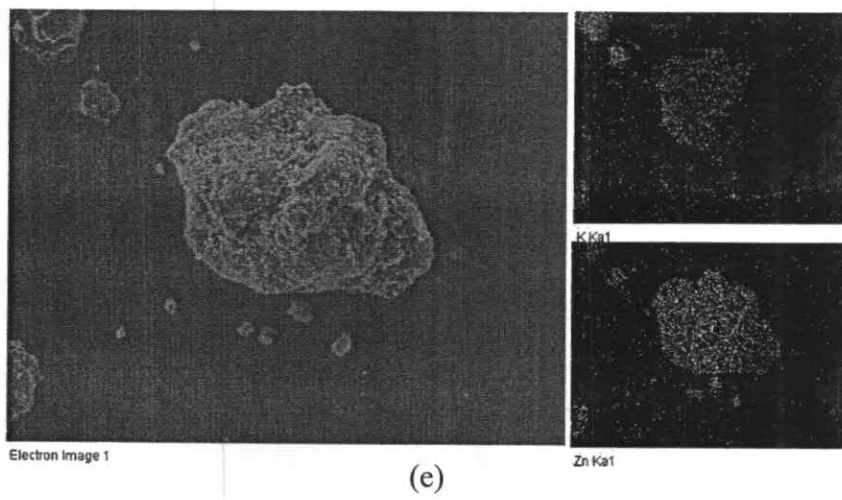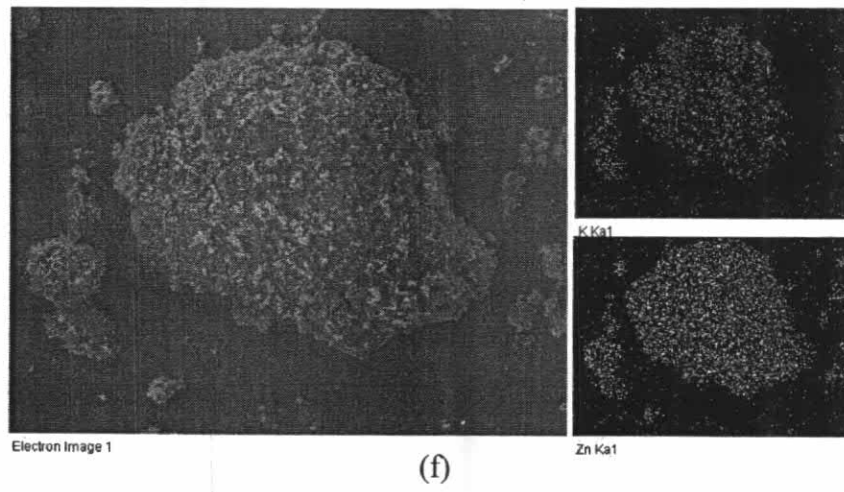
Figure 4.6 (Continued)

4.3 Transesterification Reaction

Initially, the methanol and the vegetable oil are immisible and form into two-phase system. Stirring is needed to enhance contact among the reactants. Srivastava [40] has noted that it is necessary to conduct the reaction at temperature close to the boiling point of methanol (60 to 70°C) under atmospheric pressure, in order to achieve high ester conversion. Therefore, the reaction temperature used in the experiment was fixed to 65°C. After the transesterification, the products are mixture of esters, glycerol, methanol, catalyst and mono-, di-, and triglycerides. Long period of time was needed to ensure the complete separation of the methyl ester layer from the glycerol layer. In this work, the mixture was left undisturbed overnight.

The composition of the synthesized methyl ester was determined using a Perkin-Elmer Series 8700 gas chromatograph equipped with a flame ionization detector and a capillary column OV Carbowax 20M (30m, 0.32mmID, 0.25µmdf). Raw data for vegetable oils and its methyl esters are shown in Appendix B. All methyl esters investigated appeared in the chromatogram at the retention time less than 30 min, while the peaks at the longer retention time were believed to be partially methylated esters such as mono- and di-glycerides. Comparison between the peak intensities from vegetable oil and those from the systhesized methyl esters showed that amount of methyl esters was apparently increased, with the decrease in the partially methylated esters as the transesterification proceeded. In this work, the methyl ester content (ME. content) was calculated using the compensated normalization method with internal standardization. This method uses response factors of the compounds to correct their peak area and calculate amount of analyses. Details of the calculation are presented in Appendix B.

4.4 Effects of Various Parameters on Transesterification

Screening of the heterogeneous catalysts is necessary to identify the appropriate catalyst for the transesterification of vegetable oil. It would allow several advantages such as lower production cost, environmental friendly and ease of separation of the product mixture that would lead to the simplicity of the downstream process. In this work six alkali metal salts (Li_2CO_3, Na_2CO_3, K_2CO_3, KOH, KCl and KNO_3) loaded on ZnO were tested for the transesterification of soy been oil. The experiments were performed using a methanol-to-oil molar ratio of 9:1, using a 3 wt.% of the catalyst (based on the weight of the vegetable oil), and operated at boiling point of methanol (65 °C) at atmospheric pressure.

4.4.1 Effect of Type and Amount of Alkali Metal Loaded on of Catalysts

This part of the work, catalytic activities of six catalysts were determined and compared to their surface area and basicity. The BET surface area is important characteristic of solid catalyst because it is closely related to the catalytic activity. In the previous work [10], Zhengiang et al. noted that the catalytic activity was related to the basicity of catalyst which subsequently affected the achievable content of methyl ester. Thus, in this work, the basicity of all catalysts was determined by CO_2-TPD test. The results were shown in Appendix C. Table 4.5 shows the analyzed results for surface area of bare ZnO and alkali metal salts (Li_2CO_3, Na_2CO_3, K_2CO_3, KOH, KCl and KNO_3) loaded ZnO catalyst. It indicates that the bare commercial ZnO powder possesses surface area of 4.72 m^2/g. As it is clearly presented by these data, the introduction of the alkali metal salts alters the textural properties of ZnO, remarkably decreasing the specific surface area of the catalyst. The added alkali metal salts may cover and form aggregates on the surface of catalyst, then surface area of catalyst was decreased. This result was found in all types of the alkali metal salts as shown in Table 4.5. Furthermore, surface area of the catalyst is decreased when the loading content of the salts is increased. This effect is more pronounced as the content of the alkali metal salt loading is increased (see chromatogram in Appendix C). On the other hand, activity is increased with the increase in alkali metal salt loading. So, activity does not solely depend on surface area. Moreover, based on the low surface area of

the catalysts (1-4 m^2/g), the activity of the catalyst may not affected from the surface area. Nevertheless, the results of these transesterification (Table 4.5) indicate that the loaded catalyst have much higher catalytic activity than the bare ZnO powder, even though the specific surface area is significantly smaller than that of the bare ZnO powder. This can be concluded that basicity have more effect to the activity than the surface area of the catalyst.

Table 4.5 BET surface area, basicity and catalytic activities of alkali metal salt loaded ZnO catalysts.

Catalyst	Loading amount	BET Surface Area (m²/g)	Basicity (µmol/g)	Methyl Ester Content (%)[a]
commercial ZnO	-	4.72	1.29	13.91
K$_2$CO$_3$/ZnO	15%	3.07	19.27	60.04
	20%	2.72	21.10	63.79
	25%	2.18	22.84	70.18
	30%	1.75	26.59	77.48
Li$_2$CO$_3$/ZnO	15%	1.65	11.22	35.26
	20%	1.42	12.19	36.77
	25%	1.46	15.11	39.30
	30%	1.34	18.72	42.11
Na$_2$CO$_3$/ZnO	15%	3.38	9.25	29.25
	20%	3.14	10.79	31.22
	25%	3.19	10.73	35.01
	30%	1.80	21.72	48.11
KOH/ZnO	15%	3.19	11.36	47.15
	20%	3.17	13.00	49.67
	25%	2.97	15.88	51.68
	30%	1.39	25.73	68.69
KNO$_3$/ZnO	15%	1.61	11.49	27.71
	20%	1.47	11.85	28.90
	25%	0.90	13.09	30.45
	30%	0.52	13.71	38.17

Table 4.5 (Continued)

Catalyst	Loading amount	BET Surface Area (m²/g)	Basicity (µmol/g)	Methyl Ester Content (%)[a]
KCl/ZnO	15%	3.84	0.64	11.45
	20%	3.79	0.88	12.24
	25%	2.68	1.97	14.28
	30%	2.64	3.65	15.84

[a] Methyl ester content of the product from transesterification using 3%(by weight of oil) of catalyst, molar ratio of methanol-to-oil of 9:1, reaction temperature of 65 °C, reaction time of 48 h and using THF as co-solvent.

Another factor enormously affecting the activity of the catalyst in transesterification is basicity of the catalyst. The result of this effect will be further explained. Screening tests were performed to evaluate the catalytic activity of various catalysts. The obtained results are presented in Figure 4.7. It should be noted that these reaction conditions did not represent the optimal conditions necessary to obtain the highest methyl ester content. However, they provided a way to compare catalytic activities among the catalysts. From Table 4.5, it can be seen that the unloaded ZnO exhibits the lowest catalytic activity. However, when alkali metal was loaded onto the ZnO and subsequently calcined at 600°C, the catalysts show the catalytic activity toward the soybean oil transesterification. Among all catalysts tested, it is found that ZnO loaded with K_2CO_3 has the highest catalytic activity, resulting in the methyl ester content exceeding 60% (as shown in Figure 4.7). The best catalytic activity was achieved from 30%K_2CO_3/ZnO, of which the methyl ester content reached 77.48% over 48 h. On the other hand, KCl/ZnO catalyst results in the methyl ester content lower than 20%, indicating relatively low catalytic activity. The CO_2-TPD was also used to compare the basicity characteristics of the catalysts. The basicity of various catalysts are also summarized in Table 4.5. As shown in the table, it is generally observed that high basicity results in high methyl ester content from the transesterification, as it has been acknowledged that the transesterification reaction needs highly basic sites. Nevertheless, for 30%K_2CO_3/ZnO and 30%KOH/ZnO systems, the basicities of such two systems are similar but the methyl ester contents are different. It may be caused from the difference of basic strength. Generally, the CO_2-TPD graphs of all catalysts investigated in this work as the temperature is

increased. The first peak is desorption of CO_2 slightly bonded with active site of catalyst at low temperature, which represents low basicity of the catalyst. The second peak at higher temperature represents desorption of CO_2 bonded strongly with the active site of catalyst. The higher the desorption temperature, the higher the basicity of the catalyst. It was found that the height of the peak, i.e. the basicity of the catalyst, was increased with the increase in alkaline metal salt loading, as shown in Figure 4.8. This result is in agreement with previous reports for transesterification in literatures. Zhengiang et al. [10] studied the basic strength and basicity of $Sr(NO_3)_2/ZnO$ using various Hammett indicators. They found that the basicity was increasing with $Sr(NO_3)_2$ loading. In addition, activity of the catalyst was also increasing with %salt loading. However, it should be noted that $30\%KNO_3/ZnO$ results in higher methyl ester content than $30\%Li_2CO_3/ZnO$ even though it has lower number of basic site than $30\%Li_2CO_3/ZnO$. As the result, it can be concluded that the activity of the catalyst depends not only upon the number of basic sites, but also upon the effect of surface area.
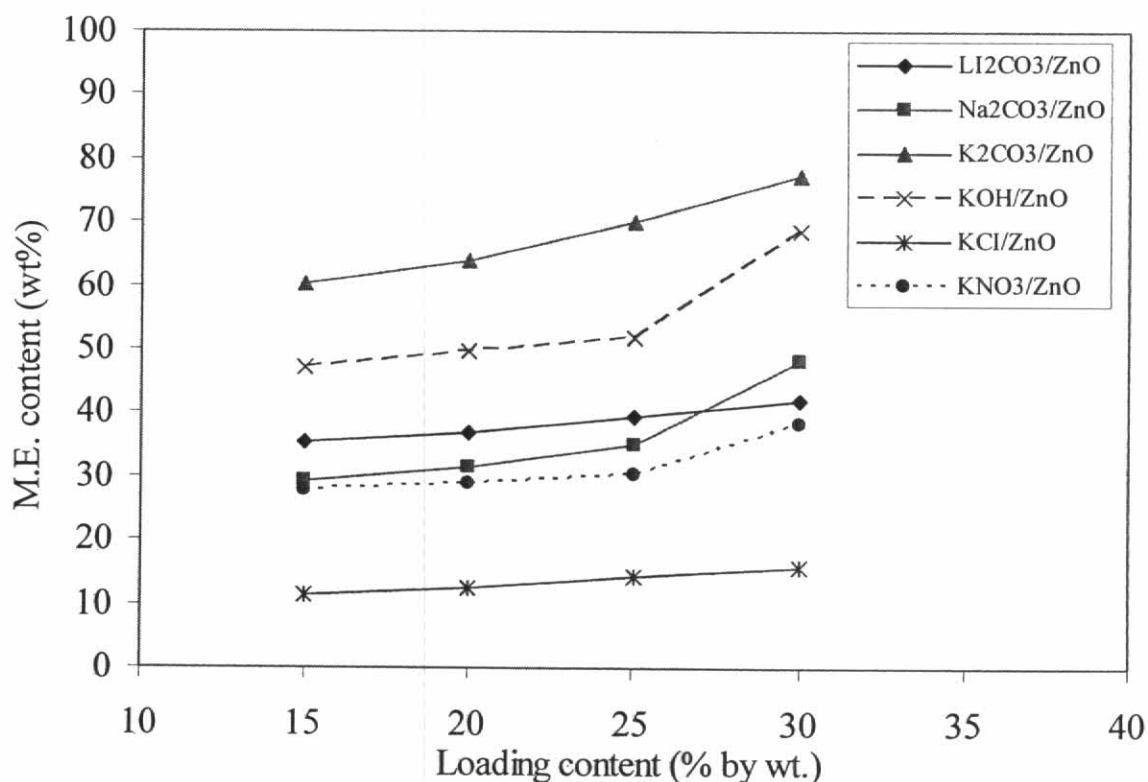
Figure 4.7 Effect of amount of alkali metal loaded on ZnO on methyl ester content of the product from transesterification using 3% (by weight of oil) of catalyst, molar ratio of methanol-to-oil of 9:1; reaction temperature of 65 °C, reaction time of 48 h and using THF as co-solvent.
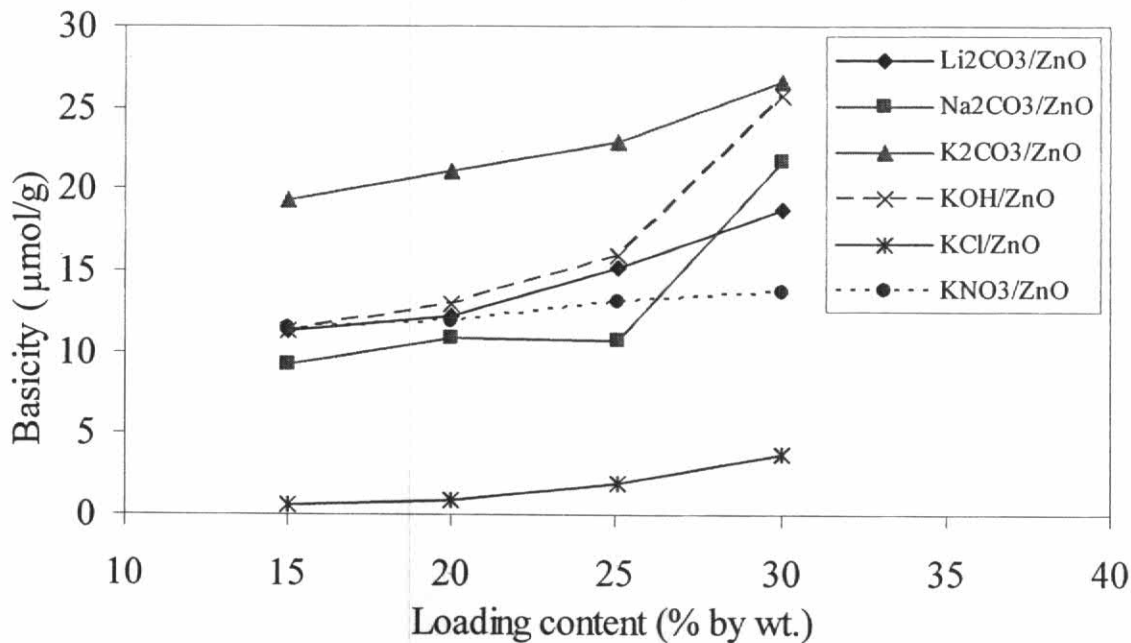
Figure 4.8 Basicity of the alkali metal loaded on ZnO samples with different loading amounts of alkali metal

The number of basic sites of the ZnO powder loaded with various alkali metal salts (Li_2CO_3, Na_2CO_3, K_2CO_3, KOH, KCl and KNO_3) with different loading amounts are given in Figure 4.8. It can be seen that when the amount of loaded K_2CO_3 is increased from 15 to 30 % by weight, the basicity is markedly increased. The results from the transesterification reaction, using these catalysts, are already presented in Figure 4.7. According to this Figure, as the amount of K_2CO_3 loading is increased from 15 to 30 %, the achieved methyl ester content is increased with the maximum value of 77.48% reached at the K_2CO_3 loading of 30 % by weight. Similar trend was observed from ZnO powder loaded with other alkali metal salts. According to Figure 4.7 and Figure 4.8, good correction between the basicities and catalytic activities of the catalysts is observed. Therefore, the activity of the catalysts is dependent on their basicity. The more the basic sites, the higher the activity of the catalysts. Since the 30%K_2CO_3/ZnO catalyst is the most active catalyst under the employed reaction conditions, it was further employed to investigate the effects of reaction parameters. Based on the XRD and FTIR characterization results of six catalysts, it was found that the alkali metal salt on surface of ZnO was formed as amorphous layer without chemical bonding between the alkali metal salt and ZnO. Therefore, the activity depends upon type of alkali metal salt, which subsequently affects basicity of the catalyst.

4.4.2 Effect of Methanol-to-Oil Molar Ratio

The molar ratio of methanol-to-oil is also considered as one of the most important variables affecting the ester content. In the transesterification, 3 moles of methanol for every mole of oil is needed to form 3 moles of methyl esters and one mole of glycerol. Xuejun et al. [39] studied this effect in the transesterification of soy been oil. They noted that, at 12:1 molar ratio, 97% yield of the ester was obtained. As as the methanol-to-oil molar ratio was decreased to the theoretical ratio of 3:1, the percentage of the ester obtained decreased to 61%. When the mass transfer is limited due to the problems from inadequate mixing, the mass transfer rate seems to be much slower than the reaction rate. Therefore the methanol-to-oil molar ratio should be higher than that of the stoichiometric ratio in order to drive the reaction towards completion and produce more methyl esters as product.

In this work the effect of methanol-to-oil ratio is shown in Figure 4.9. As shown in this figure, by increasing the amount of methanol in the reaction system, the methyl ester content in the obtained product is increased considerably. The methyl ester content is increased from 22.32% to 77.48% when the methanol-to-oil ratio is increased from 3:1 to 9:1. However, the increase in the methanol-to-oil ratio from 9:1 to 12:1 does not result in significant change in the methyl ester content. The excessive methanol can dilute catalyst to lower concentration and the content of methyl ester will be decreased. In addition, amount of methanol dissolved in glycerol layer becomes increased. This can affect the separation time of glycerol. Moreover some esters will be dissolved in methanol layer causing the amount of obtained ester to be decreased. On the contrary, the reaction mixture with the 12:1 ratio needs more processing to remove excess methanol, while for the mixture with 9:1 molar ratio, separation of methyl ester and glycerol layer can be done quickly. Therefore, the optimum value of the methanol-to-oil molar ratio to produce methyl ester is approximately 9:1.
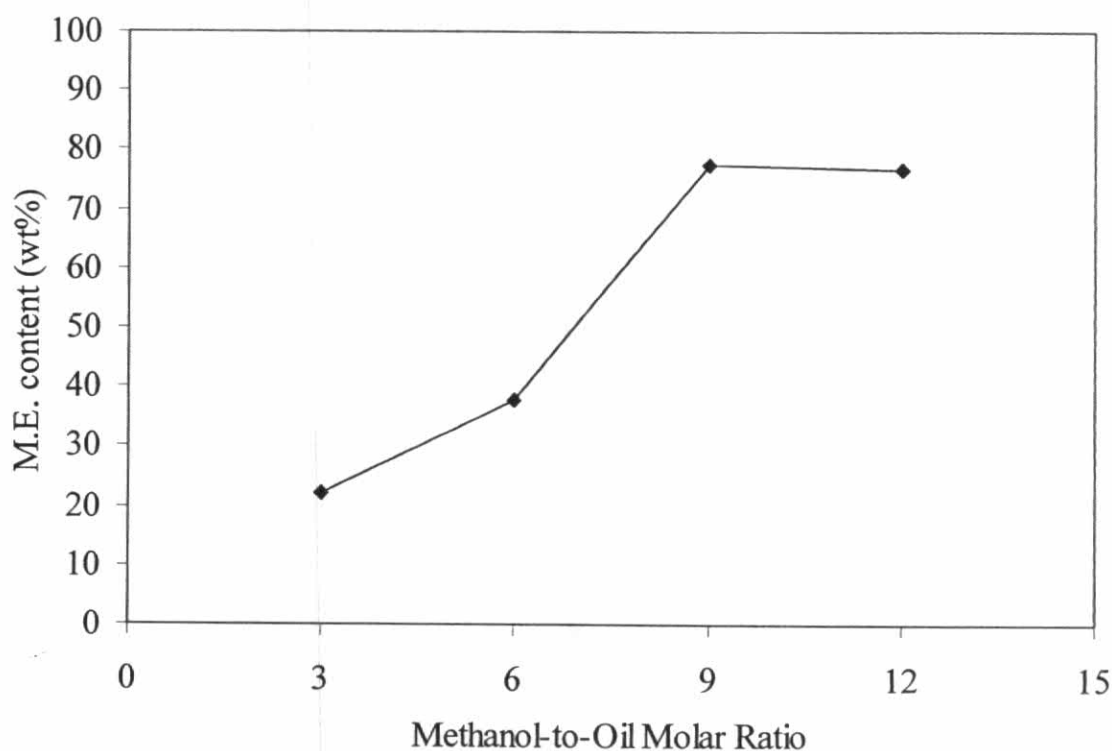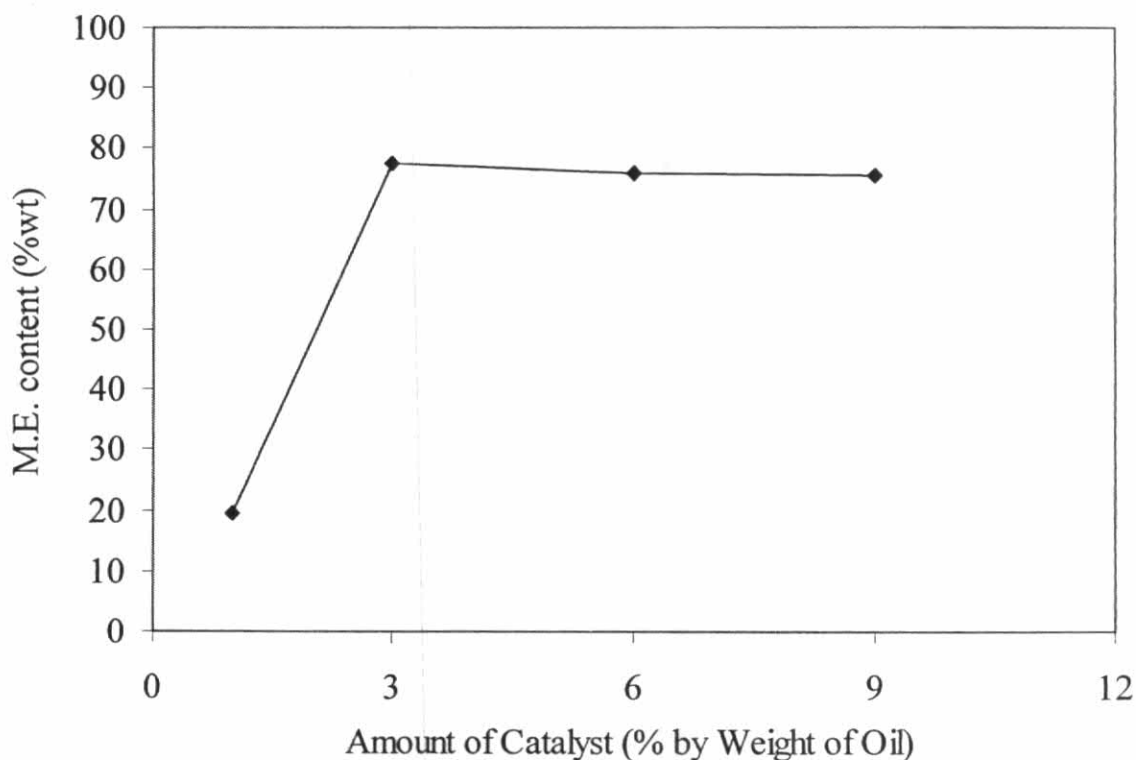
Figure 4.9 Effect of methanol-to-oil molar ratio on methyl ester content of the product from tranesterification using 3% (by weigh of oil) of 30%K$_2$CO$_3$/ZnO catalyst; reaction temperature of 65 ^{o}C, reaction time of 48 h and using THF as co-solvent.

4.4.3 Effect of Amount of Catalysts

In the case of homogeneous catalysts, it has been reported that the amount of catalysts has strong influence on the conversion to methyl esters [10]. For the heterogenous catalyst, catalyst possessing strong basic sites and a large surface area should exhibit high activity [4]. Wenlei Xie et al. [9] remarked that the transesterification reaction was strongly dependent upon the amount of catalyst applied i.e., without addition of catalyst, the transesterification did not occur, while the presence of the supported catalyst significantly increased the reaction rate. In this study, the effect of amount of catalyst loaded into the reaction system was studied by using 30%K$_2$CO$_3$/ZnO catalyst with 9:1 molar ratio of methanol to soybean oil at 65 ^{o}C for 48 h. The results are shown in Figure 4.10, in which the methyl ester content is increased from 19.52% to 75.61% by increasing the amount of 30%K$_2$CO$_3$/ZnO catalyst from 1 to 9% based on the starting oil weight. However, there is no distinct

benefit regarding the achieved methyl ester content from increasing the amount of catalyst beyond 3 %. This is possibly due to a mixing problem involving reactants, products and solid catalyst.
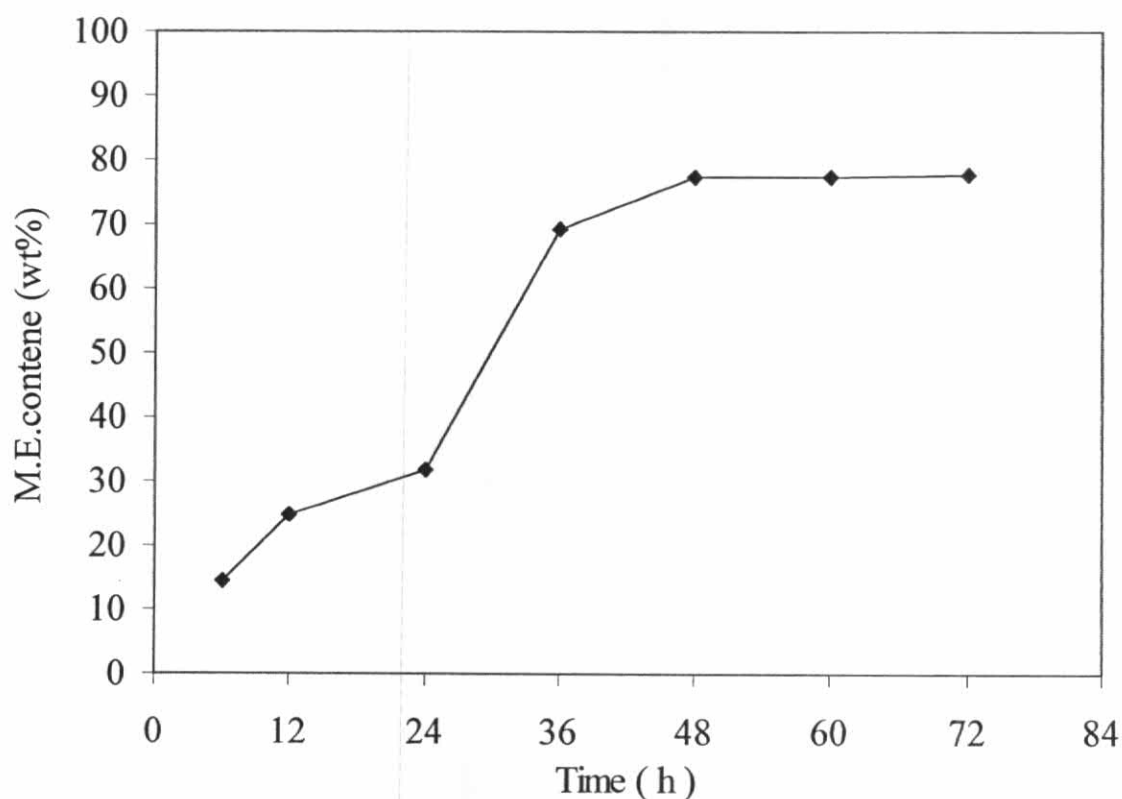

Figure 4.10 Effect of amount of catalyst on methyl ester content of the product from tranesterification using $30\%K_2CO_3/ZnO$ catalyst, molar ratio of methanol-to-oil: 9:1, reaction temperature of 65 $^{\circ}C$, reaction time of 48 h and using THF as co-solvent.

4.4.4 Effect of Reaction Time

Based on the previous work of Wenlei et al. [38], transesterification of soybean oil was performed by loading KF onto ZnO in reflux of methanol to find optimum reaction time. The result showed that optimal reaction time was 9 hrs with 87% conversion achieved. Zhengiang et al [10] studied the reaction of $Sr(NO_3)_2$ on ZnO and found the suitable reaction time for this reaction to be 5 hrs. In this work, the optimum reaction time for the production of biodiesel was determined by performing reaction at varying reaction time in the range 6-72 h. The experimental results, reported in Figure 4.11, indicated that the methyl ester content increased steadily in

the reaction time range between 6 h and 48 h, and thereafter stayed nearly constant, which was a nearly equilibrium conversion. Thus, the maximum methyl ester content of soybean oil was achieved after 48 h of reaction time. On the basis of these results, the optimum reaction time for the synthesis of biodiesel is considered to be around 48 h. Though the reaction time is relatively longer than that of the homogeneous catalysts, it does not require too much time for subsequent processing of the products, such as, neutralization, washing and drying.

Figure 4.11 Effect of reaction time on methyl ester content of the product from transesterification using 3% (by weight of oil) of 30%K_2CO_3/ZnO catalyst, molar ratio of methanol-to-oil of 9:1, reaction temperature of 65 °C, and using THF as co-solvent.

4.4.5 Effect of Organic Co-solvent

Since methanol and soybean oil are immiscible, the transesterification reaction using heterogeneous catalyst is a three-phase system. Therefore, the transesterification reaction is diffusion-controlled and the poor diffusion between phases results in a slow reaction rate. It is believed that an appropriate co-solvent that would promote oil/methanol miscibility would accelerate the transesterification by enhancing contact of the reactants with the solid catalyst. Indeed, previous reports have already shown that addition of a co-solvent can allow the transesterification reaction to proceed efficiently [10, 20, 30]. Zhengiang et al. [10] studied influence of co-solvent to the reaction by varying 3 solvents such as dimethyl sulfoxide (DMSO), n-hexane and tetrahydrofuran (THF). The result shows that THF was the most effective co-solvent and the conversion of soybean oil was increased up to 96.8% with the help of THF. THF is chosen in this study because its boiling point of 67 °C is only two degrees higher than that of methanol. Therefore at the end of the reaction the un-reacted methanol and THF can be co-distilled. According to the results shown in Figure 4.12, THF is an effective co-solvent and the methyl ester content of soybean oil can be increased up to 77.47% with the help of THF. In this case, THF can decrease mass transfer problem. THF molecule is consisted of both polar and non-polar parts. The polar part can bind with methanol while non-polar part binds with oil. So, co-solvent THF can help mixing between polar and non-polar layers of this reaction. A similar phenomenon was also observed by Karmee and Chadha [30] and Gryglewicz [22] who explained the result by considering the solubility of THF in methanol and oil which makes THF a mutual solvent. Owing to THF, the mutual oil– methanol solubility could be increased, resulting in an increase of the reaction rate.
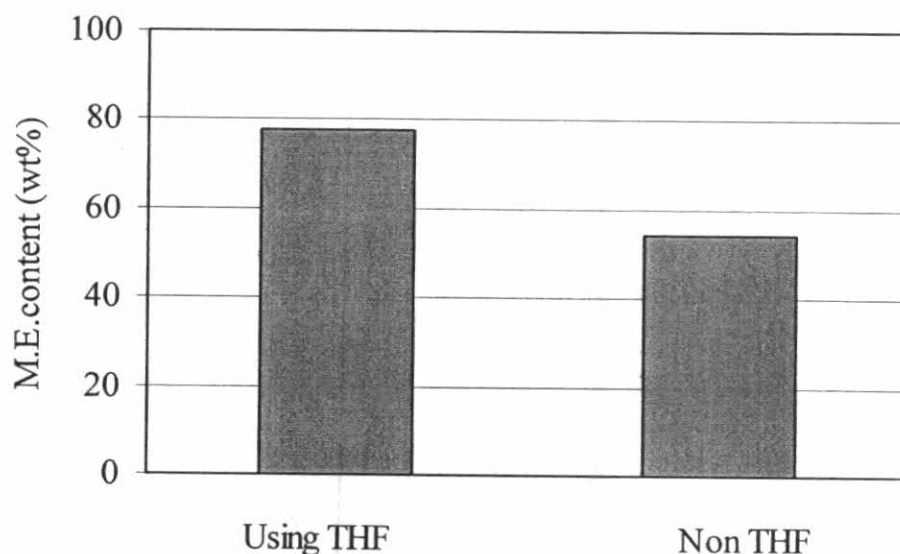
Figure 4.12 Effect of co-solvent on methyl ester content of the product from transesterification using 3%(by weight of oil) of 30%K_2CO_3/ZnO catalyst, molar ratio of methanol-to-oil of 9:1, reaction temperature of 65 °C, and reaction time of 48 h.

4.4.7 Reusability of Catalyst

In this work six alkali metal salts (Li_2CO_3, Na_2CO_3, K_2CO_3, KNO_3, KCl and KOH) were loaded on ZnO and used as are representative heterogeneous base catalysts for the transesterification of soybean oils to methyl esters. This section investigates and compares their activity after repeatedly used. The catalysts was reused by separating the catalyst, washing it thoroughly with methanol and heating in an oven for 2 h at 110°C before use in the next experiment. The results in Table 4.6 indicate that the activity of K_2CO_3/ZnO catalysts, which are the best catalyst in term of high methyl ester content, rapidly decreases during the repeated experiments. The methyl ester content is decreased from 77.47% to 34.46% and finally to 19.55% after used for three times. These results are corresponding to the decrease in the basicity, as demonstrated in Table 4.6. Most probably, the decrease in the catalytic activity can be the result from the fact that the alkali metal compounds are dissolvable in methanol. Methanol removes the active sites from the catalyst and therefore the methyl ester content achievable is decreased after the repeated uses. For ZnO loaded with other salts, similar behaviors for the methyl ester content were observed in Figure 4.13. Generally, the basicity of all catalyst investigated decreased about 40%, after used for

are time, which exhibits short catalyst lifetime, as shown in Figure 4.14. For further investigation, an additional experiment was set up under the same reaction condition, but without heating. The result shows that the basicity is not significantly decreased if the mixture is not heated. It indicated that the leaching of alkali salt from ZnO takes place at relatively high temperature. The leaching of the salt may be the result from the fact that alkali metal salt is only coated on the surface of catalyst without forming bond with ZnO. This result is similar to the previous work. Xuejun et al. [39] studied reusability of Al_2O_3 coating with K_2CO_3 and KF salts. They found that activity of the catalyst is decreased to 60% for both salt systems after 4 time usage. It can be noted that catalyst studied in this work behaves like homogeneous catalyst because of this leaching problem. Catalytic activity of the system is increased from that of the conventional heterogeneous catalyst because of alkali metal salt in the solution.

Table 4.6 Basicity and catalytic activities of $30\%K_2CO_3/ZnO$ catalysts

| Catalyst	Basicity (μmol/g)	Methyl Ester Content(%)[a]
Fresh catalyst	26.59	77.48
After used for 1 time	13.51	34.46
After used for 2 times	3.29	19.55
After reaction without heating	23.94[b]	N.A.

N.A.: not analyzed.

[a] Methyl ester content of the product from transesterification using 3%(by weight of oil) of catalyst, molar ratio of methanol-to-oil of 9:1, reaction temperature of 65 °C, reaction time of 48 h and using THF as co-solvent.

[b] determined after reaction.
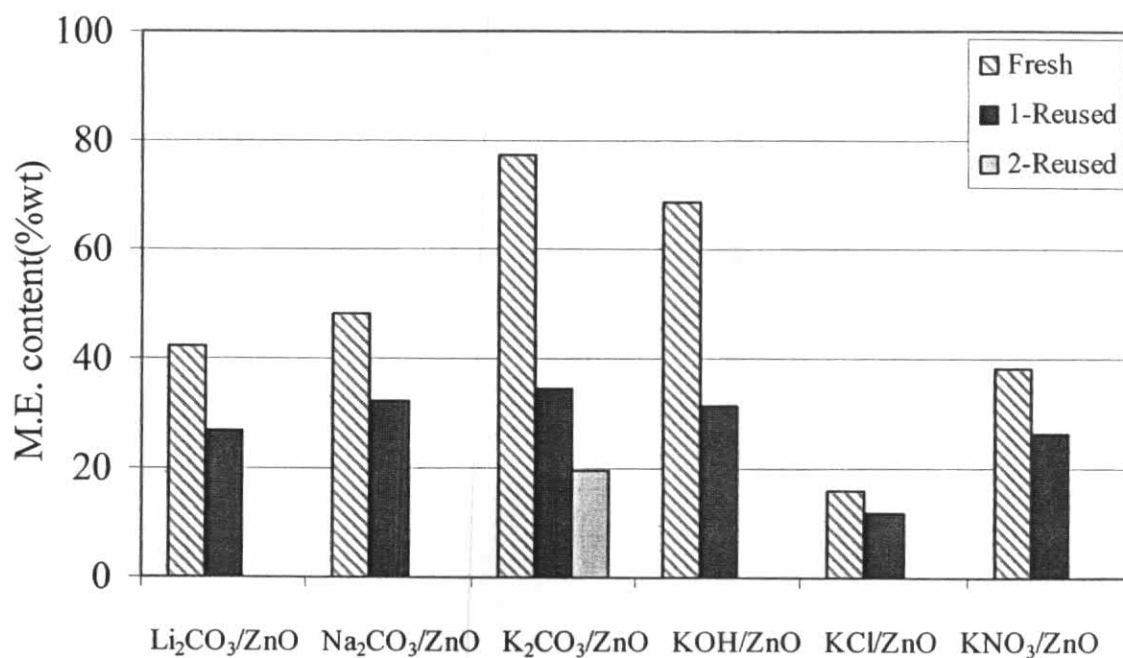
Figure 4.13 Methyl ester content of the product from transesterification using 3% (by weigh of oil) of reused catalyst, molar ratio of methanol-to-oil of 9:1, reaction temperature of 65 °C, reaction time of 48 h and using THF as co-solvent.
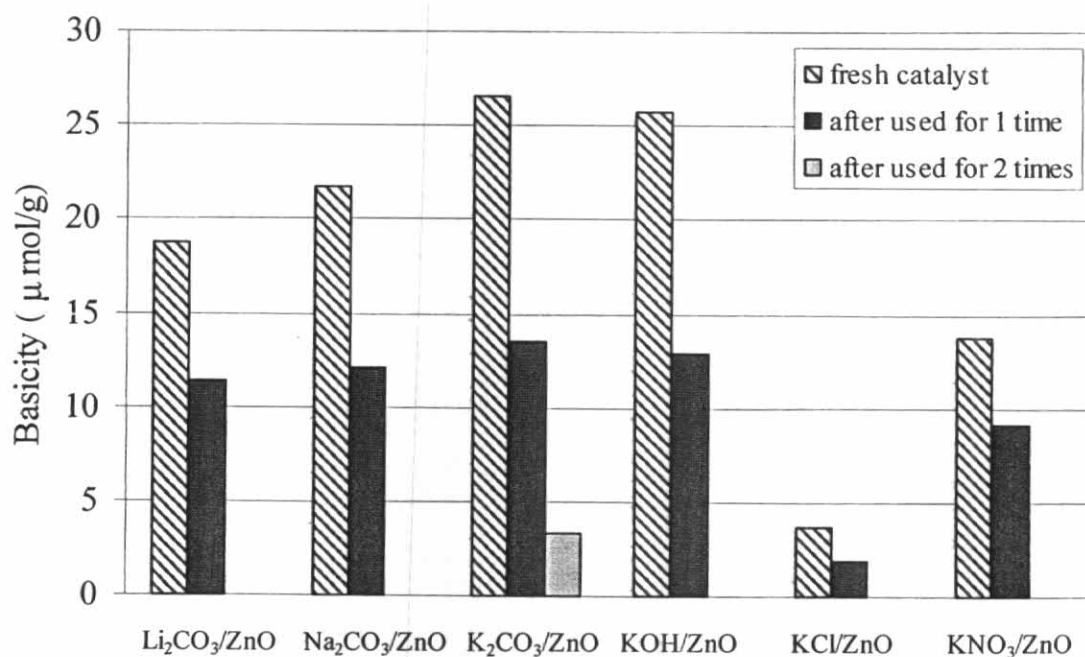
Figure 4.14 The basicity of catalyst after repeated experiments as using 3% (by weigh of oil) of catalyst at; molar ratio of methanol to oil: 9:1; reaction temperature: 65 °C; reaction time: 48 h and THF as a co-solvent.

4.5 Transesterification Using ZnO Synthesized by Solvothermal Method

The studies in the previous sections have shown that the commercial ZnO powder loaded with30% K_2CO_3 is the most active catalyst among all catalysts investigated. In this regard the 30%K_2CO_3 loading was farther applied to the ZnO powder synthesized by the solvothermal method and compared with that of the commercial ZnO catalysts, for the transesterification of soybean oil to methyl esters under the optimal condition determined previously.

## 4.5.1 Characteristic of ZnO Prepared by Solvothermal method

In this part, the solvothermal method was employed to synthesize ZnO nanorods. This technique is based on thermal decomposition of organometallic compound in organic solvent and has been successfully applied for the synthesis of various types of nanosized metal oxide with large surface area, high crystallinity and high thermal stability. Tonto et al. [12] prepared ZnO nanorods by solvothermal reaction of zinc acetate in toluene at 250-300°C for 2 hours. All products were ZnO having the hexagonal wurtzite structure. No impurity or secondary phase was observed. These conditions were chosen for the synthesis of ZnO in this experiment.

Figure 4.15shows the typical X-ray diffraction patterns of the commercial ZnO powder and ZnO prepared by solvothermal method. All diffraction peaks of the products can be well indexed as a pure hexagonal ZnO structure, which are in agreement with the literature values (JCPDS Card Number 36-1451). Furthermore, the strong intensity of diffraction peaks of ZnO synthesized via the solvothermal technique indicates that the resulting products have high crystallinity.
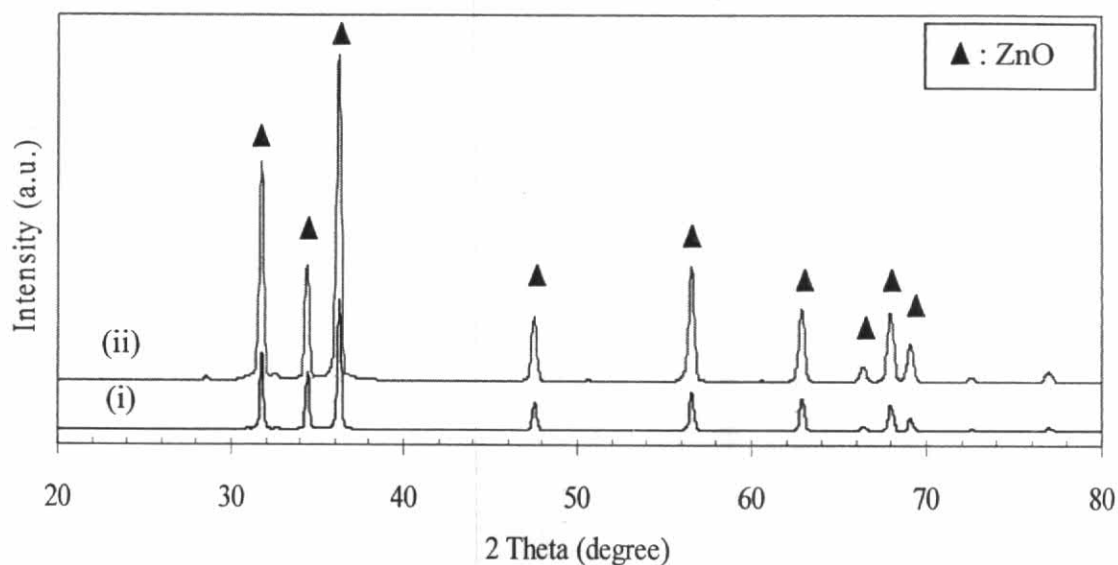
Figure 4.15 XRD patterns of: (i) commercial ZnO powder and (ii) ZnO synthesized by the solvothermal method.

Scanning electron microscopy was used to examine of the topology of catalyst surfaces. Figure 4.16 shows the SEM images of the commercial ZnO comparing with ZnO synthesized by the solvothermal method. It is clearly illustrated that morphology of particles synthesized by the solvothermal technique in toluene is significantly different from commercial ZnO. The commercial ZnO particles are ellipsoidal (Figure 4.16(a)) while the rod-like particles (Figure 4.16(b-c)) were observed in the ZnO prepared by the solvothermal technique. Each rod-like particle is longer than 10 μm in length and smaller than 100 nm in diameter. Most of these particles congregate to form conglomerations. The catalyst crystal itself is solid without observable pores. Large pores (1000–1500 nm) are located between the agglomerates with the pore volume of 0.023 cm^3/g in the catalyst (raw data are summarized in Appendix C).

(a)

(b)

(c)
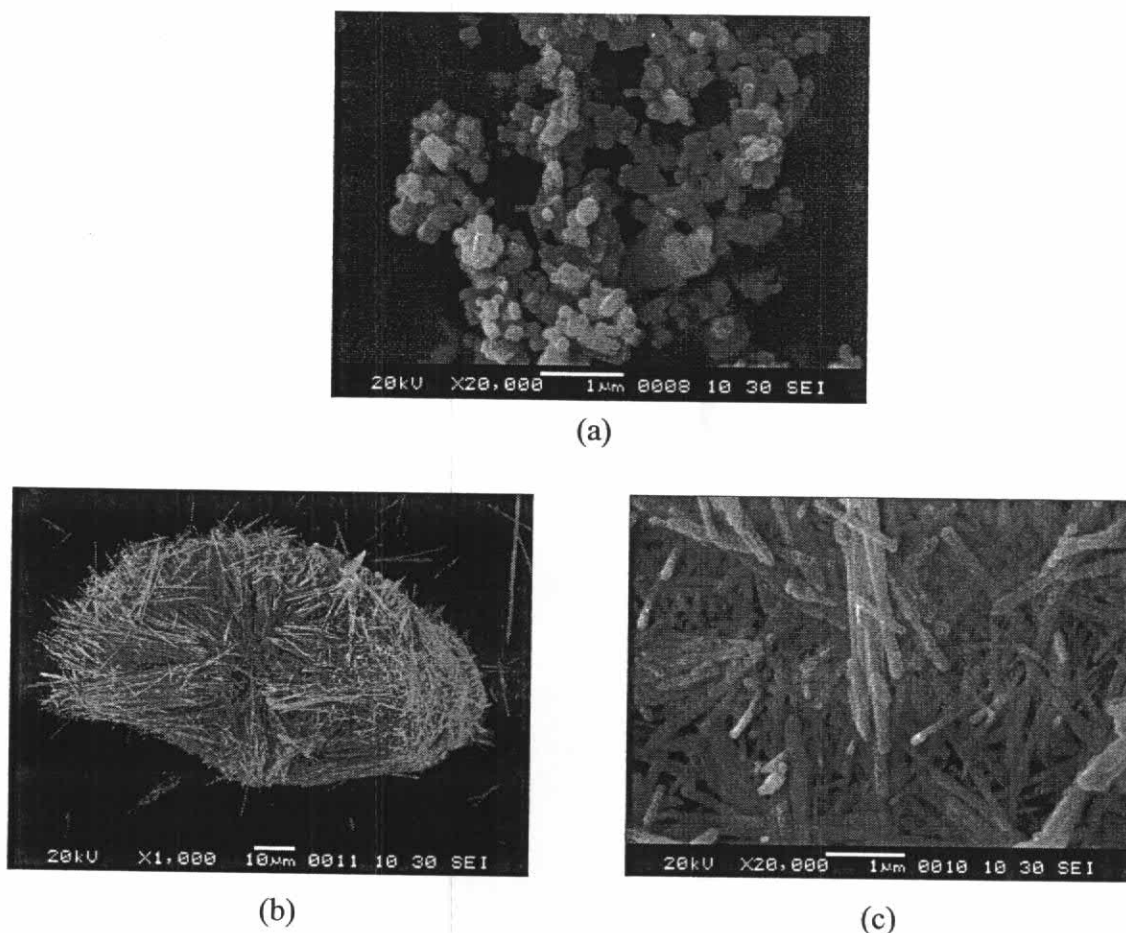
Figure 4.16 Scanning electron micrographs (SEM) of: (a) commercial ZnO and (b-c) ZnO synthesized by solvothermal method.

4.5.2 Catalytic Activities

Table 4.7 shows the BET surface of the commercial ZnO, ZnO synthesized by the solvothermal method and powder loaded with 30% K_2CO_3. It indicates that the surface area of ZnO synthesized by the solvothermal technique is higher than the commercial ZnO catalyst, i.e. 7.63 m^2/g and 4.72 m^2/g, respectively. However, when K_2CO_3 were loaded onto the ZnO and subsequently calcined at 650°C for 5 h, the supported catalysts showed dramatically improved catalytic activities towards the soybean oil transesterification, for both type of ZnO powder. Furthermore, The CO_2-TPD was used to compare the amount of basic sites on these catalysts, as summarized in Table 4.7. As shown in the table, the K_2CO_3 loaded ZnO ,which was synthesized by the solvothermal method, has the high basicity of 33.77 μmol/g and results in high methyl ester content of 80.66%, while the 30% K_2CO_3 loaded commercial ZnO

possessed the lower basicity, (26.59 μmol/g) and thereby, exhibiting lower catalytic activities. According to these data, the activity of the catalyst depends upon the basicity characteristics in greater extent than the surface area of the catalyst. It is interesting that the synthesized ZnO, processing higher specific surface area but lower in basicity, gave better catalytic activity. Therefore, it clearly suggested that the surface area have a pronounce effect on the catalyst performance.

Table 4.7 BET surface areas, basicity and catalytic activities of ZnO catalysts.

Catalyst	BET Surface Areas (m²/g)	Basicity (μmol/g)	Methyl Ester Content(%)[a]
Commercial ZnO	4.7166	1.29	13.91
ZnO synthesized by solvothermal method	7.6302	1.26	16.81
30%K_2CO_3/ZnO (commercial)	2.1802	26.59	77.48
30% K_2CO_3/ZnO (synthesized by solvothermal method)	N.A.	33.77	80.66

N.A.: not analyzed.

[a] Methyl ester content of the product from transesterification using 3%(by weight of oil) of catalyst, molar ratio of methanol-to-oil of 9:1, reaction temperature of 65 °C, reaction time of 48 h and using THF as co-solvent.